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THE DETERMINATION OF MERCURY

BY

C. M. BOUTON and L. H. DUSCHAK

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CONTENTS.

	Page.
Introduction	5
Apparatus	6
Analytical procedure	8
Distillation	8
Titration	9
Modified procedure when organic matter or much sulphur is present	9
Procedure when sulphur is present	9
Procedure when organic matter and sulphur is present	9
Procedure for assaying a filtered precipitate	10
Device for feeding tubes into assay furnace	11
Alternative procedure for refractory samples	11
Determination of mercury in solution	11
Experiments	12
Accuracy of distillation procedure	13
Effects of evolution of gas	15
Possibility of retention of mercury by the charge	16
Trial assay with sulphur and organic matter present	18
Interfering elements	19
Titration	20
The Eschka method	22
Acknowledgment	23
A bibliography on analytical methods for the determination of mercury	24
Gravimetric and precipitation methods	24
Precipitation of free mercury	24
By zinc	24
By copper	24
By brass	25
By stannous chloride	25
By alkali arsenite	25
By formaldehyde	25
By chloral hydrate	25
By hydrazine or hydroxylamine	25
Precipitation of calomel	26
By organic reagents	26
By ferrous sulphate and alkali	26
By phosphorous acid	26
By stannous chloride	27
By sulphur dioxide	27
By hydrogen peroxide and ammonium tartrate	27
By sodium chloride	27
Precipitation of mercuric sulphide	27
Precipitation of mercuric iodide	28
Precipitation of ammonium derivatives	28
Other precipitates	28
Volumetric methods	29
Direct titrations	29
With potassium iodide	29
With potassium cyanide	30
With potassium thiocyanate	30
With stannous chloride	30
With sodium chloride	31
With sodium thiosulphate	31
With potassium permanganate	31
With potassium iodate	31
With ammonia	31

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A bibliography on analytical methods for the determination of mercury—Con.
Volumetric methods—Continued. Page.
Indirect and residual titrations 32
Acidimetric 32
Alkalimetric 32
Iodimetric 32
By permanganate 34
By cyanide 34
By thiocyanate 34
By chloride 34
Colorimetric methods 34
As mercuric sulphide 34
As mercuric diphenyl carbazide 34
Distillation methods 35
Distillation in a tube not sealed at either end 35
Distillation in a tube sealed at one end 35
Distillation in a crucible covered by a cooled gold or silver top 36
Miscellaneous 37
Methods of solution of mercury-bearing materials 37
Other miscellaneous methods 38
List of authors 39
List of subjects 41
Publications on metallurgy 42

TABLES.

Page.
TABLE 1. Results of simple distillation of mercury in closed tube 13
2. Results of distillation of mercury in tubes with sand plug 14
3. Results of assays of synthetic sulfide ore 15
4. Results of distillation of mercury in a current of air 15
5. Results of distillation of mercury over metallic copper 17
6. Results of assays of material containing sulphur and organic matter 18
7. Results of assays with arsenic, antimony, selenium, and tellurium present 19
8. Results of assays of calomel 20
9. Results showing effects of chloride salt on the titration of mercuric salt with potassium thiocyanate 21
10. Results of standardizations of potassium thiocyanate solutions with silver and mercury 22

ILLUSTRATIONS.

Page.
PLATE I. *A*, Steps in making wire gauze plug; *B*, Transferring distillation tube to nitric acid tube for solution of distilled mercury 6
II. *A*, General view of quicksilver assay furnace; *B*, Placing sample in distillation tube; *C*, Automatic feeding device for distillation tubes. 7
FIGURE 1. Details of iron block for quicksilver assay furnace 7

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THE DETERMINATION OF MERCURY.

By C. M. Bouton and L. H. Duschak.

INTRODUCTION.

The method described in this report was developed by the Bureau of Mines for use in a study of mercury condenser losses,[a] and especially for the determination of minute amounts of mercury associated with organic matter. A preliminary description of the method has been published in Bulletin 78 of the California State Mining Bureau.[b]

Almost without exception the volumetric methods described in the literature (see the bibliography at the end of this article) are based on the use of tenth-normal solutions for titration. Hence with the customary analytical technique a variation of about one milligram of mercury may be detected, or, if one gram of material be taken for assay, the mercury content may be determined within 0.1 per cent. As a considerable part of the world's mercury is obtained from ores carrying less than 1 per cent mercury, an analytical procedure that will quickly and accurately detect a variation of less than one milligram of mercury is much to be desired.

Of the numerous volumetric methods tested, the method of titration with potassium thiocyanate, using ferric sulphate or nitrate as indicator, proved to be the only one capable of the desired refinement. This titration is vitiated by the presence of any halide. Therefore in bringing the mercury of the sample into solution a method must be employed which absolutely excludes all halogen compounds. Briefly, the analytical procedure finally adopted consists in separating the mercury by distillation in a closed tube, dissolving it in nitric acid, and titrating with thiocyanate. With slight modification the method can be applied to the determination of mercury in practically any material, including that containing considerable quantities of organic matter.

With readily provided facilities one operator can make 50 to 60 determinations in an eight-hour day, and with an assistant at least 100 samples can be run, exclusive of the time required for crushing and grinding the samples.

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[a] **Duschak, L. H., and Schuette, C. N., Fume and other losses in condensing quicksilver from furnace gases: Tech. Paper 96, Bureau of Mines, 1918, 29 pp.; Min. and Sci. Press, vol. 117, 1918, p. 315.**

[b] **Bradley, W. W., Quicksilver resources of California: Bull. 78, Calif. State Mining Bureau, 1918, pp. 278-280.**

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APPARATUS.

Distillation of the mercury from the sample is accomplished in a straight tube of pyrex or similar "hard" glass, about 22 cm. long and not over 10 mm. in external diameter. One end is sealed by drawing to a conical tip; a little bead of glass is left at the tip to facilitate opening the tube when the distilled mercury is to be dissolved.[a] The same tube may be used many times by resealing the end.

In order to retain the powdered ore and reagents in place in the tube, plugs made of pieces of 50-mesh brass gauze about 12 mm. wide by 18 to 25 mm. long are used. The different steps in preparing these plugs are shown in Plate I, *A*. In one of the longer edges of the gauze four equidistant incisions about 5 mm. deep are made. The gauze is then bent around a piece of small tubing into the form of a cylinder, and the flaps are bent inward, closing the cylinder at the bottom. A piece of nichrome wire, about 28 B. & S. gage and about 3 cm. long, is woven into four holes, punched with a needle in the gauze, in such a way as to leave two small loops projecting from the walls of the cylinder. These loops are bent along the cylinder walls toward the open end of the cylinder. Nichrome retains considerable elasticity at the temperature of the furnace, and the plug, inserted with the closed end against the charge, holds its position in spite of the expansions and contractions attending the temperature changes. Several dozen plugs should be ready for use. Before the plug is inserted, the nichrome wire should always be bent out a little to make sure that it will grip the walls of the tube. Satisfactory plugs can no doubt be made from nichrome gauze if this material is available. The brass plugs are good for 10 to 20 assays. For reasons explained below asbestos plugs are not satisfactory.

A rod of soft steel 3 or 4 mm. in diameter and about 40 cm. long, provided with a short sharp lateral spur at one end, serves to draw the brass plugs from the tubes. For an occasional assay a combustion furnace or other convenient device may be used for heating the tubes, but when a considerable number of determinations are to be made, a cast-iron block with a number of holes, as shown in Plate II, *A*, and in figure 1, is recommended. This block may be heated electrically or with a Meker burner or Dangler gasoline torch. With either of these latter methods the burner, or torch, should be protected by asbestos board from the strong downward radiation of heat. The temperature of the block should be between 450° and 550° C.

[a] A method of mercury assaying based on distillation in a closed tube and followed by collecting the distilled mercury on gold beads under cyanide solution has been in use in California for many years. This method is mentioned by S. B. Christy ("Quicksilver condensation at New Almaden," Trans. Am. Inst. Min. Eng., vol. 14, 1885, p. 206), and, according to information privately communicated by Mr. Walter L. Gibson, of Oakland, Calif., was devised by Mr. Louis Falkenau and his partner, Mr. Reese, of San Francisco, about 1877–78.

The determination of minute amounts of mercury by distillation in a closed tube has also been worked out by P. E. Raaschou (Eine mikrochemische Quicksilberbestimmungs Methode, Ztschr. Anal. Chem., Jahrg. 49, 1910, p. 172). Raaschou suggests the possible application of his procedure to technical ore analysis.

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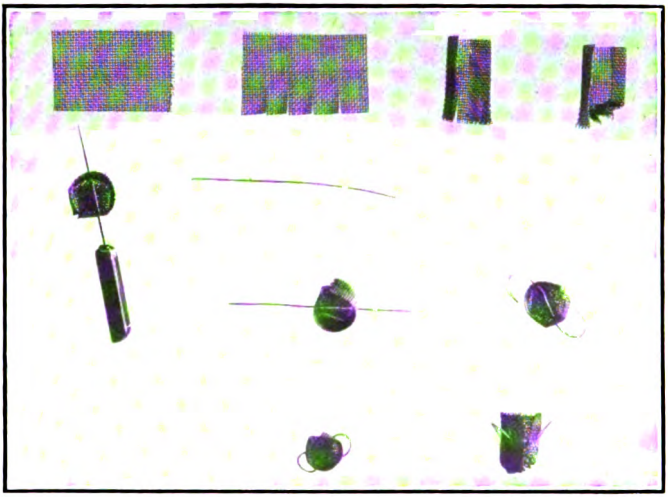
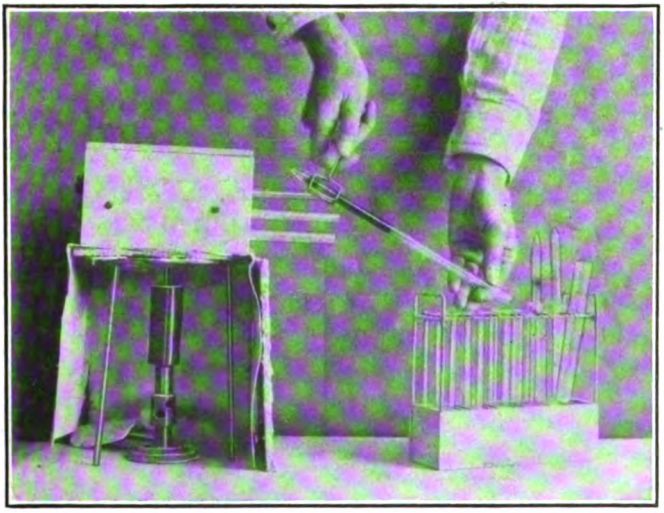


A. FIRST STEPS IN MAKING WIRE GAUZE PLUG.



B. TRANSFERRING DISTILLATION TUBE TO NITRIC ACID TUBE FOR SOLUTION OF DISTILLED MERCURY.

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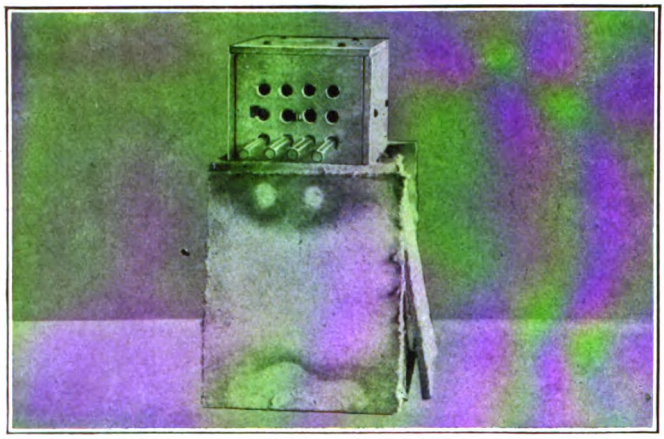
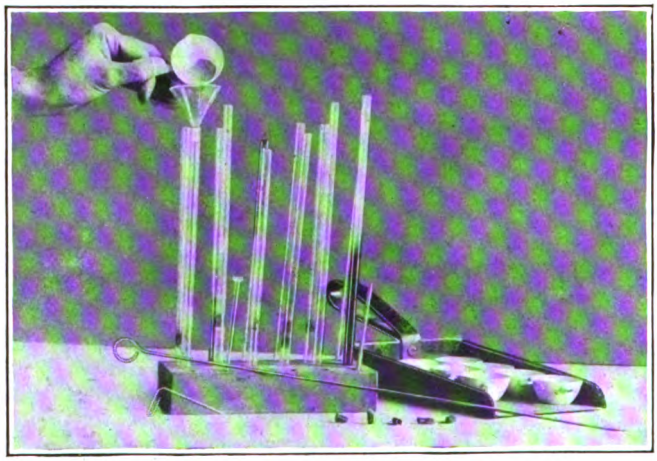
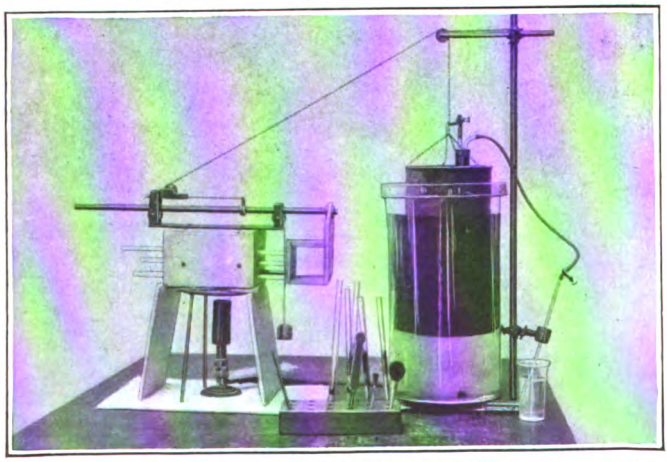


A. GENERAL VIEW OF QUICKSILVER ASSAY FURNACE.



B. PLACING SAMPLE IN DISTILLATION TUBE.



C. AUTOMATIC FEEDING DEVICE FOR DISTILLATION TUBES.

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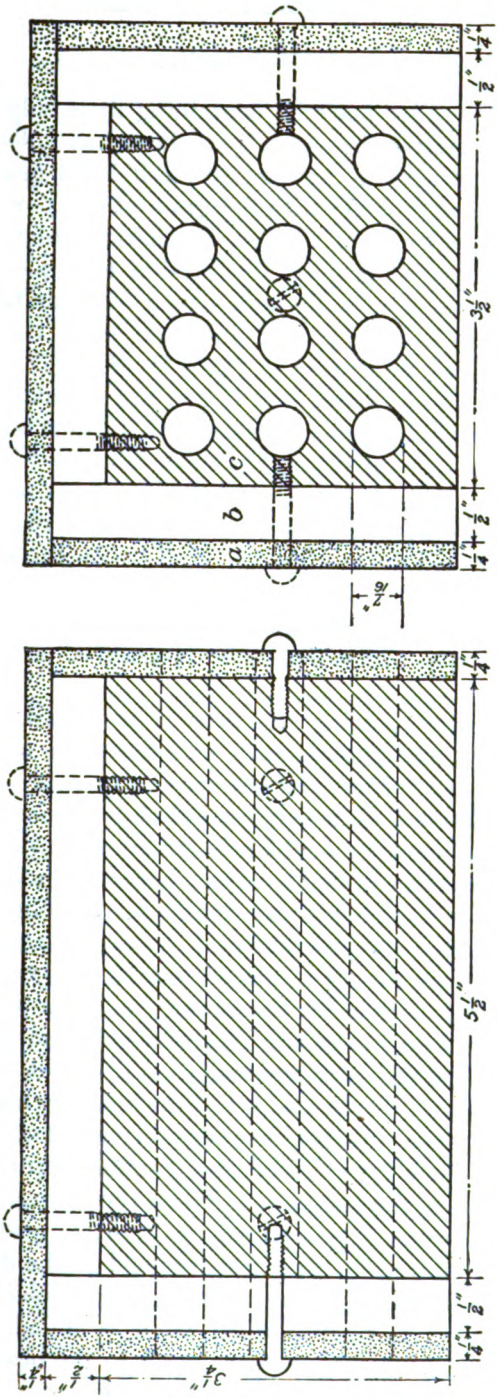

FIGURE 1.—Details of iron block for quicksilver assay furnace.

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ANALYTICAL PROCEDURE.

DISTILLATION.

With an ore or other material containing little sulphide, free sulphur, or organic matter the assay is conducted as follows:

The sample is crushed to at least 80 mesh and 1 gram is mixed in a small casserole or crucible with 0.5 gram of dry powdered calcium oxide. The conical end of a glass distillation tube is filled with coarse sand or crushed granite, the portion that passes a 10-mesh screen and is retained on a 20-mesh screen being suitable. The ore and lime mixture is then poured into the tube, through a short-stemmed funnel, as illustrated in Plate II, *B* (p. 7). If the ore is rich in mercury, the casserole and funnel are sprinkled with a little lime, and both are thoroughly brushed with a camel's-hair brush. A 1-cm. layer of lime is poured into the tube, followed by a like layer of the coarse sand. A brass gauze plug of a suitable size is selected, the nichrome loops are bent slightly outward, and the plug is inserted in the tube and pressed down upon the sand by means of the iron rod. The tube is turned horizontally and tapped lightly upon the table, so as to form above the ore charge a small channel through which the vapors may escape. Then the tube is inserted in the previously heated iron block.

After 15 minutes' heating the tube is withdrawn, as shown in Plate I, *B* (p. 6), and placed, open end down, in a test tube containing about 5 c. c. of hot concentrated nitric acid. The test-tube rack, shown in Plate I, *B*, is constructed of galvanized iron and iron wire. A layer of sand 1 cm. thick is spread over the bottom of the box, making a sand bath which may be heated on a hot plate.

When the tube has cooled sufficiently for handling, the bead at the tip of the closed end is broken off, leaving a small opening. A piece of soft rubber tubing is placed over this opening and gentle suction is applied, either by the mouth or by a water aspirator, drawing the hot acid above the ring of condensed mercury. Care must be taken that the nitric-acid solution does not come in contact with the metal plug. If the acid is hot the mercury rapidly dissolves, emitting brown fumes. It should be borne in mind that if too cool, nitric acid attacks mercury very slowly, and a small drop of mercury may remain unnoticed in the test tube. When the mercury is completely dissolved, the solution is poured into a 100-c. c. beaker, care being taken that a column of liquid is not retained in the distillation tube by capillarity. The distillation tube is then replaced in the test tube, and 10 to 15 c. c. of distilled water is added. The water is drawn up by suction and then transferred to the beaker. A second such washing removes all mercury to the beaker.

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TITRATION.

In order to oxidize all mercury to the mercuric state, a moderately strong solution of potassium permanganate is added, drop by drop, until a permanent color is produced. The excess of permanganate is then destroyed by a drop or two of hydrogen peroxide. For the indicator, 2 c. c. of a 10 per cent solution of ferric sulphate or nitrate is added. This must be absolutely free from chloride or other halides. If anhydrous ferric sulphate is used in preparing the indicator, considerable heating is necessary to obtain a clear solution.

For titration the mercury solution should be cool and the volume preferably not over 30 c. c. If it is judged that the amount of mercury present is less than 50 mg., the solution is titrated with a hundredth normal solution of potassium thiocyanate; if more than 50 mg. of mercury is present, a tenth normal solution is more convenient. The first distinct pink color marks the end point. The thiocyanate solution may be standardized by dissolving weighed amounts of mercury in nitric acid and proceeding as described, or weighed amounts of pure mercuric oxide may be used.

MODIFIED PROCEDURE WHEN ORGANIC MATTER OR MUCH SULPHUR IS PRESENT.

PROCEDURE WHEN SULPHUR IS PRESENT.

When the sample contains elemental sulphur, pyrite, or other source of free sulphur, some sulphur vapor may accompany the mercury vapor, giving rise to a deposit of mercuric sulphide with the condensed mercury. This will be indicated by a discoloration of the mercury and particularly by a black residue remaining undissolved by nitric acid. It has been found that with material containing as much as 20 per cent of free sulphur a satisfactory distillation can be made by adding powdered cupric oxide to the granular calcium oxide with which the sample is mixed. When as much as 20 per cent sulphur is present, two parts of cupric oxide are used to one part of lime. With lesser amounts of sulphur the proportion of cupric oxide is reduced.

PROCEDURE WHEN ORGANIC MATTER AND SULPHUR IS PRESENT.

Bituminous material is not infrequently associated with mercury ores. Various metallurgical products, such as mercurial soot and flotation concentrates, also contain organic matter. When any considerable amount of organic material is present, a distillate of organic liquids may form with the mercury in the fore part of the distillation tube. It has not been observed that this interferes with the subsequent titration with thiocyanate except in so far as the yellow or brown

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color which the organic matter may impart to the solution masks the end point.

Interference due either to an excessive amount of sulphur or to organic matter may be obviated by the following procedure:

A distillation tube about 30 cm. long is used. A small quantity of potassium chlorate, not exceeding by weight 10 per cent of the quantity of ore taken for test, is mixed with the sand used for filling the conical end of the tube; in addition to the 1 gram of lime, the sample is mixed with 1 to 2 grams of powdered cupric oxide and 0.1 to 0.3 gram of powdered chlorate, according to the amount of material to be oxidized. The charge prepared as above is poured into the tube and is followed by 2 to 4 cm. of a mixture of roughly equal volumes of finely granular cupric oxide and lime. The usual cap of coarse sand and the gauze plug follow. The length of the whole charge, measured from the bottom of the tube to the top of the plug, should not exceed 13 cm.

For the distillation an asbestos plug is withdrawn from the rear of a hole in the assay furnace; then the tube is inserted in the usual manner, except that it is passed back until only the copper oxide and lime layer remains in the iron block, the rest of the charged tube projecting from the rear of the furnace. After about three minutes the tube is fed slowly forward, 0.5 to 1 cm. at a time, care being taken to avoid any sudden rush of gas. In this way a slow evolution of oxygen from the potassium chlorate is obtained, and the organic material, sulphides, and sulphur are almost entirely oxidized. Much of the carbon dioxide and much of the sulphur dioxide produced are absorbed by the lime and only a slow current of gas, chiefly the gaseous hydrocarbons of low molecular weight and the excess oxygen, escapes from the tube. When the closed end of the tube has finally been fed into the furnace, the asbestos plug is once more inserted behind the tube; heating is continued five minutes longer to give any mercury condensed in the tip time to diffuse to the front of the tube. Then the assay is concluded as usual.

PROCEDURE FOR ASSAYING A FILTERED PRECIPITATE.

A mercurial precipitate contained on a filter paper may be assayed according to the procedure just outlined. The paper and contents are first dried at a low temperature to avoid volatilization of mercury compounds. If the precipitate is bulky, it is advisable to remove the major portion of the precipitate from the filter paper and mix this portion separately with the reagents. Any part of the filter paper entirely free from precipitate should, of course, be rejected. What remains is rolled into a cylinder and inserted in a tube already charged with 0.5 to 0.8 gram of potassium chlorate mixed with a little fine sand as a diluent. The filter paper is followed by as long

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a column of copper oxide and lime as will fall within the 13 cm. limit for total length of charge. These latter materials should be screened free from all dust finer than about 80 mesh, to assure the necessary porosity.

DEVICE FOR FEEDING TUBES INTO ASSAY FURNACE.

This type of assay requires constant attention during the feeding of the tube into the furnace. If a large number of such assays are to be made, a mechanical device for feeding the tubes into the furnace saves time. Such a device is illustrated in Plate II, *C* (p. 7). Its construction will be fairly clear from the photograph. The motive power is derived from the slow sinking of a diving bell, in this case a bottomless tin can weighted at the lower edge and protected from rusting by a coat of asphaltum paint. The sinking is regulated by the escape of air through the rubber tube provided with a screw pinchcock, and the escaping air is bubbled through a small column of water in order to observe the rate of escape. The motion is communicated to the rod and suspended "pusher" by a light brass chain and pulleys. The small weight, shown suspended in the rear of the furnace, serves to hold the rod and pusher taut against the pull of the chain.

ALTERNATIVE PROCEDURE FOR REFRACTORY SAMPLES.

An alternative procedure which may be followed when the sample contains troublesome ingredients is to bring it into solution and follow the method outlined below for solutions. Organic matter may be destroyed by the Kjeldahl digestion method or by other means employed in physiological analysis. As pointed out by Treadwell,[a] it is not safe greatly to concentrate by evaporation a solution of mercury containing strong hydrochloric acid, as a loss of mercury may occur through the escape of mercuric chloride vapor. The writers' own experiments confirmed this statement and also showed that there is much less danger of loss in evaporating solutions containing only sulphuric or nitric acids or both.

DETERMINATION OF MERCURY IN SOLUTION.

Except in special assays where some simple procedure is possible, it is believed that the best method of determining mercury in solution is to precipitate with hydrogen sulphide and treat the precipitate by the method previously outlined. When only a small amount of mercury is present, the addition of a few drops of copper sulphate solution before precipitation with hydrogen sulphide, as recommended

[a] Treadwell, F. P., Analytical chemistry, vol. 2, 3d ed., 1912, p. 168.

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by Raaschou,[a] facilitates the collection and handling of the precipitate.

For assays where the precipitation with H_2S in acid solution would result in the formation of a large amount of free sulphur, the method of precipitation proposed by Volhard [b] may be employed.

The precipitate may be collected on an ordinary filter, which after drying is treated by the method described for materials containing sulphur and organic matter. A better method, however, which avoids the use of potassium chlorate and the more elaborate distillation process, is to collect the precipitate upon a film of clay previously deposited in an alundum filtering crucible. A 20-c. c. alundum crucible is placed under suction and filled with a suspension containing 1 gram of only moderately plastic clay to 100 c. c. of water. The mercuric sulphide is then collected in this crucible, care being taken that in filtration the solution does not rise above the upper edge of the clay deposit on the sides of the crucible. After washing, the crucible is dried in an air bath. The mercuric sulphide, together with most of the clay, can then be readily removed by the use of a thin knife blade.

As will be shown later, very few substances interfere with the determination of mercury by the distillation method, thus making it possible to perform the mercury determinations with a special portion of the original solution and without any previous separation of other substances present. For the same reason, although the use of H_2S as a precipitant is usually preferable, any convenient method of precipitating the mercury may be employed.

EXPERIMENTS.

In developing the analytical method outlined above, various alternative procedures have been tested and possible sources of error investigated. Some of the experiments that establish the probable accuracy of the method tested and indicate the various precautions necessary are described in the following paragraphs.

In the majority of these experiments a known weight of mercury, which had been carefully purified by distillation in air under partial vacuum, was employed. Approximately 40 mg., corresponding to 40 c. c. of a hundredth-normal solution of potassium thiocyanate was the quantity usually taken, as this was convenient for titration and corresponded to conditions for minimum experimental error in the ordinary volumetric procedure. This small amount of mercury was conveniently obtained by the use of a medicine dropper having a capillary tip about 4 cm. long and a shallow bulb blown into one side

a Raaschou, P. E., Eine mikrochemische Quecksilberbestimmungs Methode: Ztschr. anal. Chem., Jahrg. 49, 1910, pp. 172-204.

b Volhard, J., Ueber Krystallisirtes Quecksilberoxychloride und die Bestimmung des Quecksilbers: Ann. der Chemie, Bd. 255, 1889, p. 255; Treadwell, F. P., Analytical Chemistry, vol. 2, 3d ed., 1912, p. 169.

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just above the tip to serve as a receptacle for the drop of mercury during weighing. A few trials served to calibrate the tip roughly so that any desired quantity of mercury could be easily obtained. Two weighings of the dropper were made in every test.

In some tests, where it was desired to work with a known amount of mercury in the form of mercuric sulphide, weighed quantities of metal were dissolved in nitric acid and precipitated with hydrogen sulphide. The precipitate was collected on a clay film in an alundum crucible as described on page 12.

ACCURACY OF DISTILLATION PROCEDURE.

In order to determine the accuracy with which mercury can be distilled and condensed in a glass tube closed at one end, a weighed quantity of mercury was dropped to the bottom of one of the distillation tubes previously described and this was placed in the iron block furnace which had been previously heated to about 500° C. Heating was continued for about 15 minutes, after which the usual analytical procedure was completed. The results of these tests are shown in experiments 1 to 13, Table 1. It will be noted that with approximately 40 mg. of mercury a fairly consistent loss of about 0.3 mg. is recorded. The use of a plug of cotton in the mouth of the tube in experiments 7 and 8 did not materially alter this result. Experiments 9, 10, and 11 show that the loss is roughly proportional to the quantity of mercury employed. In all these tests the tubes employed extended 7 to 12 cm. beyond the furnace. On the other hand, experiments 12 and 13, in which a tube projecting 30 cm. beyond the furnace was employed, showed a recovery complete within the experimental errors of weighing and titration.

TABLE 1.—*Results of simple distillation of mercury in closed tube.*

Experiment No.	Quantity of mercury taken for test.	Quantity of mercury recovered.	Error.	Remarks.
	Gram.	*Gram.*	*Mg.*	
1	0.0404	0.0401	−0.3	Open tube.
2	.0407	.0404	− .3	Do.
3	.0420	.0417	− .3	Do.
4	.0408	.0405	− .3	Do.
5	.0398	.0395	− .3	Do.
6	.0405	.0401	− .4	Do.
7	.0391	.0388	− .3	Cotton in mouth of tube.
8	.0385	.0383	− .2	Do.
9	.0030	.0029	− .1	Open tube.
10	.0107	.0104	− .3	Do.
11	.3566	.3535	−3.1	Do.
12	.0401	.0399	− .2	Tube projected 30 cm. beyond furnace.
13	.0424	.0424	.0	Do.
14	.0410	.0410	.0	Sealed tube.
15	.0393	.0393	.0	Do.
16	.0323	.0323	.0	Do.
17	.0394	.0393	− .1	Do.

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In experiments 14 to 17, Table 1, a longer tube sealed at both ends was used. The tubes used in Nos. 14 and 15 were sealed under atmospheric pressure; in Nos. 16 and 17 the air pressure was reduced to 550 and 140 mm. of mercury, respectively, before sealing. In experiments 14 and 15 all of the mercury condensed within 15 cm. and in Nos. 16 and 17 within 9 cm. of the front of the furnace.

It is evident from these latter experiments that mercury may be quantitatively distilled along a glass tube and also that the manipulation of dissolving the condensed mercury and preparing it for titration does not involve any sensible error. On the other hand, with the shorter open tubes a persistent loss of mercury is noted and the failure to eliminate this by the use of a cotton plug indicates that convection currents of air circulating in the tube are not responsible for the loss.

It seemed possible that the loss might be due to mercury vapor carried away by the rapidly expanding air within the tube, this air under the conditions of experiment being increased to more than two and one-half times its original volume. The rapid evaporation of the mercury, owing to the quick heating of the empty tube, would favor loss in this way.

The correctness of this explanation is indicated by the experiments recorded in Table 2, in which a filling of crushed granite of the size indicated was placed above the mercury in the bottom of the tube and held in place by the usual brass gauze plug. The sand filling reduced the volume of air to be expelled and also decidedly reduced the rate at which the mercury distilled.

TABLE 2.—*Results of distillation of mercury in tubes with sand plug.*

Experiment No.	Quantity of mercury taken for test.	Quantity of mercury recovered.	Error.	Fineness of sand filling (metric screen scale).	
				Through.	On.
	Gram.	*Gram.*	*Mg.*	*Mm.*	*Mm.*
1	0.0396	0.0395	−0.1	0.85	0.5
2	.0336	.0337	.1	.5	.25
3	.0396	.0396	.0	.17	.14
4	.0419	.0417	−.2	.14	.105
5	.0414	.0414	.0	.105	.074
6	.0151	.0151	.0	.105	.074
7	.0405	.0406	.1	.1	.074
8	.0412	.0411	−.1	.5	—
9	.0420	.0419	−.1	.5	—

These experiments settle conclusively the accuracy of the fundamental procedure on which the method is based. The accuracy of the method with material free from organic matter and containing little sulphur is further shown by experiments recorded in Table 3, in which a known amount of mercury was converted to sulphide as outlined and was analyzed according to the standard procedure.

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TABLE 3.—*Results of assays of synthetic sulfide ore.*

Experiment No.	Quantity of mercury taken for test.	Quantity of mercury found.	Error.
	Gram.	*Gram.*	*Mg.*
1	0.0045	0.0044	−0.1
2	.0263	.0261	− .2
3	.0441	.0442	.1
4	.0831	.0828	− .3
[a]5	.2227	.2214	−1.3
[a]6	.4806	.4799	− .7

[a] Solution in Nos. 5 and 6 was titrated with 0.1 normal KSCN solution.

EFFECTS OF EVOLUTION OF GAS.

In certain types of assay, when the sample contains carbonates, sulphur, or organic matter, evolution of gas may take place. It is therefore necessary to determine the probable loss of mercury when condensed from a moving current of gas. The first five experiments listed in Table 4 were performed by placing a drop of mercury in a column of lime and copper oxide in a combustion tube, such as is used for organic analysis, and heating gradually in a gas combustion furnace. About 200 c. c. of air or oxygen were passed in a slow, steady current during the whole time of heating. The recovery of mercury is well within the experimental errors of weighing and titration.

TABLE 4.—*Results of distillation of mercury in a current of air.*

Experiment No.	Quantity of mercury taken for test.	Quantity of mercury recovered.	Error.	Air current.	
				Velocity.	Total volume.
	Gram.	*Gram.*	*Mg.*	*Cm. per sec.*	*C.c.*
[a]1	0.2602	0.2600	−0.2	.....	200
[a]2	.0194	.0193	− .1	.....	200
[a]3	.0153	.0153	.0	.....	200
[a]4	.0168	.0166	− .2	.....	200
[a]5	.1800	.1801	.1	.....	200
6	.0427	.0424	− .3	0.2	90
7	.0376	.0373	− .3	.4	180
8	.0380	.0376	− .4	.2	90
9	.0385	.0382	− .3	.2	90

[a] Results by W. C. Riddell, chemical engineer, Bureau of Mines.

Experiments 6 to 9, Table 4, were conducted as nearly as possible according to the modified procedure recommended for materials containing sulphur and organic matter. A fine capillary tube was sealed onto the closed end of one of the regular distillation tubes, the conical tip was filled with an asbestos plug, and a weighed globule of mercury was placed upon this asbestos, a short plug of sand being added in some cases. The tubes were heated in the iron block

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furnace, the current of air through the tube being established before the end of the tube containing the mercury was drawn back into the furnace.

An appreciable error was found in the results of these tests. This error was presumably due to the fact that the tube heated up quickly, causing the mercury to distill rapidly with an attendant high concentration of mercury vapor during a brief period. In actual determinations the rate of distillation is less rapid than in these last experiments, owing to the fact that a considerable length of tube is filled with solid material. Moreover, the volume of gas escaping from the distillation tube is not likely to be as great as that from the charge used in the tests. Even with a sample high in organic matter, rarely more than 0.3 gram $KClO_3$ will be required. From this amount of reagent about 100 c. c. of oxygen, measured at room temperature, would be evolved. Part of this oxygen, however, would be used up in oxidizing sulphur and carbonaceous matter, and the writers have found that nearly all of the CO_2 and SO_2 thus formed is absorbed by the lime.

A small amount of mercury vapor, corresponding to the vapor pressure of the metal at the temperature of condensation, is unavoidably carried away by the gas stream. If the extreme assumptions be made that gas leaves the distillation tube saturated with mercury vapor at 50° C., and that the gas volume at this temperature is 200 c. c., the total mercury loss,—0.0127 mm. being taken as the vapor pressure of mercury at 50° C.—would be less than 0.04 mg., a negligible amount.[a]

In assays where an evolution of gas is expected, it seems safe to conclude that error due to loss of mercury in the escaping gas can be reduced to a point well within other experimental errors by taking the necessary precautions. A longer tube than usual should be employed, and the heating should be sufficiently slow to avoid rapid evolution or sudden puffs of gas. Results of some trial assays are given in a subsequent part of this report (p. 18).

POSSIBILITY OF RETENTION OF MERCURY BY THE CHARGE.

In the early experiments, a plug of asbestos fiber was used to retain the charge in the tube. Although many satisfactory test assays were made using asbestos plugs, low results were sometimes obtained which could not be traced to any other cause and were attributed to the resistance offered by the plug to the diffusion of the mercury vapor. Occasionally an asbestos plug was forced into the forward part of a tube or the hot end of the tube expanded into

[a] Knudsen, M., Ein absolutes Manometer; Ann. der Physik, Bd. 32, Folge 4, 1910, pp. 809–842. Duschak, L. H., and Schuette, C. N., Fume and other losses in condensing quicksilver from furnaces gases, Tech. Paper 96, Bureau of Mines, 1918, p. 26.

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a bulb, showing the existence of considerable pressure. On account of the uncertainty of adjusting asbestos plugs that would remain firmly in place and yet possess the necessary porosity, the wire gauze plug already described was adopted.

Aside from the direct retention of mercury vapor in the charge, a tight plug may lead to error in another way in determinations where the use of potassium chlorate is necessary. On one occasion a deposit of mercuric oxide was found in the distillation tube about 5 cm. from the closed end. A calculation made from Pélabon's [a] work on the dissociation of mercuric oxide showed that with a tight plug the necessary conditions for the formation of oxide could easily be present. Theoretically, as the gas gradually escapes through the plug, the mercuric oxide should dissociate, and with prolonged heating all the mercury present should be transferred to the cool part of the tube. It is, however, much better to avoid any possible error from this source by the use of a plug of considerable porosity.

The possibility that mercury might be absorbed and retained by the brass gauze plug or by metallic copper arising from the copper oxide used when sulphur or organic matter is present was foreseen and tested by experiments summarized in Table 5. The usual distillation tubes were used. In the closed end of each tube a weighed droplet of mercury was placed, this being followed by a short plug of sand. In experiment 1, a 3-cm. plug of finely divided metallic copper, obtained by reducing granular copper oxide by heating with oxalic acid, was used. In experiments 2 and 3, tightly wound spirals of brass and of copper gauze, respectively, 6 to 7 cm. long were used. These were reduced by methyl alcohol, according to the usual method in organic analysis. Experiment 2 is the only one that shows significant loss. In consideration of the fact that in practice the brass gauze plug is always tarnished, and that the total amount of brass and metallic copper present is much less than that present in these experiments, it seems safe to conclude that no important error can arise from this source.

TABLE 5.—*Results of distillation of mercury over metallic copper.*

Experiment No.	Quantity of mercury taken for test.	Quantity of mercury recovered.	Error.	Remarks.
	gram.	*gram.*	*mg.*	
1	0.0423	0.0421	−0.2	3-cm. plug of fine reduced copper used.
2	.0433	.0428	− .5	6-cm. plug of brass gauze used.
3	.0403	.0403	.0	6-cm. plug of copper gauze used.
4	.0712	.0714	+ .2	2-cm. plug of fine reduced copper used.
5	.0383	.0381	− .2	Do.

[a] Pélabon, H., Sur la dissociation de l'oxyde de mercure: Compt. rend., t. 128, 1899, p. 825.

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TRIAL ASSAY WITH SULPHUR AND ORGANIC MATTER PRESENT.

The assays recorded in Table 6 following were carried out according to the modified procedure previously outlined, in which one or more oxidizing agents are employed. One of the essential conditions in making this type of assay is to bring the copper oxide layer, preceding the sample, to the temperature of the assay furnace before the heating of the sample is begun.

TABLE 6.—*Results of assays of material containing sulphur and organic matter.*

Experiment No.	Quantity of mercury taken.	Quantity of mercury recovered.	Error.	Substance added.		Reagents.
				Kind.	Quantity.	
	Gram.	*Gram.*	*Mg.*		*Gram.*	
1	0.0453	0.0454	+0.1	Sulphur.....	0.1	CaO and CuO.
2	.0498	.0497	− .1	.....do.....	.1	Do.
3	.0252	.0253	+ .1	Gilsonite.....	.1	Do.
4	.0252	.0253	+ .1	.....do.....	.1	Do.
5	.0376	.0372	− .4	Asphaltum....	.05	CaO, CuO, and $KClO_3$.
6	.0431	.0429	− .2	.....do.....	.05	Do.
7	.0411	.0407	− .4	.....do.....	.05	Do.

In experiments 1 and 2 a weighed quantity of mercury (about half a gram) was converted to sulphide, manipulated as already described, and 0.1 gram of sulphur added in addition to the cupric oxide, but no potassium chlorate was used. In experiments 3 and 4 a siliceous ore, which had been repeatedly assayed and found to contain 2.52 per cent mercury, was used. One gram of this ore was mixed with 0.1 gram gilsonite, also some lime and copper oxide, but no potassium chlorate.

In experiments 5, 6, and 7 there were used in each test a known weight of mercury in the form of mercuric sulphide, 0.05 gram of asphaltum, some lime and copper oxide, and 0.2 gram of potassium chlorate. It will be noted that in these three experiments a slight loss of mercury apparently took place. By the use of longer distillation tubes and a little more care in heating to avoid rapid evolution of gas it is believed that this loss could have been reduced to a negligible amount.

The writers' experience with the method as applied to substances with and without sulphur and organic matter indicates that in ordinary routine assaying, when no great care is taken, the loss of a few tenths of a milligram of mercury may occur. Where a considerable number of samples are being assayed according to a regular routine, the operator should carefully standardize his particular procedure, and, if necessary, apply the slight correction indicated.

Where a high degree of accuracy is desired and speed is not an important consideration, careful observance of the precautions

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already indicated will bring any error in distillation well within the limit of other experimental errors.

INTERFERING ELEMENTS.

It remains to be considered whether in addition to sulphur and organic matter certain other substances may not interfere with the assay. Elements either themselves volatile or forming compounds volatile in the vicinity of 500° C. are naturally to be suspected. In Table 7 there are recorded the results of a number of assays of a siliceous ore containing very little sulphur to which various substances were added.

When lime alone was mixed with the sample containing either the sulphides or oxides of arsenic or antimony, low and erratic results were obtained. When, in addition to the lime, cupric oxide was mixed with the sample, correct results were obtained. The precise way in which arsenic and antimony compounds interfere with the assay is not known, but they evidently belong to the group of substances that require an oxidizing agent in order to obtain correct assay.

As regards selenium and tellurium, it will be noted that substantially correct results were obtained when lime alone was mixed with the sample.

TABLE 7.—*Results of assays with arsenic, antimony, selenium, and tellurium present.*

Experiment No.	Addition substance or substances.	Quantity added, grams.	Other reagents used.	Percentage of Hg found.
1	Sb_2S_3 and Sb_2O_3	0.05 each	CaO and CuO	2.51
2	do	.15 each	do	2.50
3	do	.25 each	do	2.50
4	As_2S_3	.1	do	2.51
5	do	.2	do	2.52
6	do	.3	do	2.49
7	Selenium	.1	CaO	2.52
8	Tellurium	.1	do	2.55
Mean of six assays on ore alone				2.52

A few assays were made of mercurous and mercuric sulphates and chlorides. When lime alone was used as the reagent, low and erratic results were obtained. This was evidently due to incomplete distillation of the mercury, as the addition of water to the residues in the distillation tubes produced the characteristic red and brown colors of basic mercury compounds. There was no evidence of the distillation of the acid radicles. With these materials the use of copper oxide was without avail, but when a mixture of clean iron filings and lime was used, the expulsion of mercury from the sample

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was complete. Table 8 contains two assays of ordinary "C. P." calomel, the exact purity of which is unknown.

TABLE 8.—*Results of assays of calomel.*

Experiment No.	HgCl taken, grams.	Hg found.	
		Grams.	Per cent.
1.....	0.0517	0.0438	84.7
2.....	.4039	.3410	84.4
Mean.....			84.55
Theoretical proportion of Hg in HgCl.....			84.96

In assaying compounds of mercury such as the chlorides or sulphates, evidently a reducing rather than an oxidizing agent is needed. The use of iron filings as a reducing agent appears to have been first suggested by Eschka [a] for the release of mercury from sulphur-bearing ores. Further reference to the Eschka method is made on pages 22 to 23.

The literature reveals that much difficulty has been found in the assaying of various complex mercury-bearing substances, hence in special instances some combination of reagents other than that already suggested in this report may be necessary. For example, in assaying a material containing chloride or sulphate and organic matter, the sample itself might be mixed with lime and iron filings, as just recommended, and a layer of lime and copper oxide be placed in front of this mixture in the distillation tube. In some determinations, as already suggested, decomposition in the wet way, followed by the precipitation of mercury as sulphide, may be the most acceptable procedure.

TITRATION.

Volhard [b] in his classical paper on the titration of silver (and indirectly of halides) by means of thiocyanate, notes that mercury interfered with the titration of silver, but states that titration of mercury in the absence of silver was of approximate accuracy only. Some time later Rupp and Krauss [c] showed that in the presence of a considerable excess of nitric acid the titration of mercury is exact. Knox [d] confirms this statement, provided all mercury is present in

a Eschka, A., Beschreibung des Verfahrens zur Bestimmung des Quecksilbers in seinen Erzen: Oest., Ztschr. Berg.-Hüt., Jahrg. 26, 1872, p. 67.

b Volhard, J., Die Anwendung des Schwefelcyammoniums in der Maassanalyse: Ann. der Chemie, Bd. 190, 1878, p. 1.

c Rupp, Erwin, and Krauss, Ludwig, Ueber die maassanalytische Bestimmung von Quecksilber, sowie Quecksilber und Silber: Ber. Deut. chem. Gesell., Jahrg. 35, 1902, p. 2015.

d Knox, Joseph, The volumetric estimation of mercury and the estimation of silver in the presence of mercury: Jour. Chem. Soc., vol. 95, 1909, p. 1768.

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the mercuric state. He also calls attention to the fact that when mercuric oxide is dissolved in cold dilute nitric acid, a small amount of mercurous salt may be formed. It is well known that the solution of metallic mercury by nitric acid yields a certain amount of mercurous salt.

It is, therefore, necessary to take some definite step to oxidize all the mercury to the mercuric condition, and also to destroy any nitrous acid present. For this purpose Rupp [a] recommends the use of potassium permanganate, the excess permanganate to be destroyed by ferrous sulphate. The writers have found hydrogen peroxide equally effective for removing the excess of permanganate and without influence on the titration.

The titration of mercuric salt with potassium thiocyanate depends on the formation of slightly dissociated mercuric thiocyanate, and not on the formation of an insoluble compound, as in the case of silver. As the coefficient of ionization of mercuric chloride is of the same order of magnitude as that of the thiocyanate, chlorides, and other halides will interfere with the titration. Some quantitative data are presented in Table 9 following:

TABLE 9.—*Results showing effects of chloride salt on the titration of mercuric salt with potassium thiocyanate.*

Experiment No.	NaCl solution added.		Chlorine in NaCl solution added, mg.	Equivalent weight of mercuric chloride, mg.	Quantity of mercury taken, mg.	Mercury not detected, mg.
	Volume, c. c.	Strength.				
1	1	N/100	0.355	1.00	39.3	−1.1
2	1	N/1000	.036	.10	39.7	− .4
3	.5	N/1000	.018	.05	41.9	− .2
4	.1	N/1000	.004	.01	41.1	− .1

A minute trace of chlorides apparently causes a disproportionate error. This emphasizes the necessity of completely excluding chloride in the titration. When any chloride is present, the appearance of the end color is more gradual; this is also true of the presence of bromide or iodide.

Volhard [b] states that copper, zinc, cadmium, thallium, tin, lead, arsenic, antimony, bismuth, manganese, and iron do not interfere with the titration of silver by potassium thiocyanate, and that cobalt and nickel interfere only to the extent that their colors obscure the end point. This statement applies as well to the titration of mercury.

The solution in which the titration is carried out should be cool. Otherwise the yellow color of the iron indicator, which is more pronounced in a warm solution, will somewhat obscure the end point.

[a] Rupp, E., Ueber die maassanalytische Bestimmung des Quecksilbers nach rhodantitrimetrischem maassanalytische, jodometrischem, und acidimetrischem Verfahren: Chem. Ztg., Jahrg. 32, 1908, p. 1077.
[b] Volhard, J., place cited.

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The potassium thiocyanate solution may be standardized with either mercury or silver. Some standardizations of tenth and hundredth normal thiocyanate solutions are given in Table 10 following:

TABLE 10.—*Results of standardizations of potassium thiocyanate solutions with silver and mercury.*

Experiment No.	Approximate normality of solution.	Metal used.		Potassium thiocyanate solution used, c. c.	Normality of solution.
		Kind.	Weight, grams.		
1	0.1	Silver.....	0.2150	19.8	0.1007
2	.1	.....do.....	.3812	35.2	.1003
3	.1	.....do.....	.4663	43.1	.1002
4	.1	Mercury.....	.2056	20.45	.1006
5	.1	.....do.....	.3618	36.1	.1002
6	.1	.....do.....	.4571	45.55	.1003
7	.01	Silver.....	.0268	24.25	.01028
8	.01	.....do.....	.0371	33.9	.01014
9	.01	.....do.....	.0496	45.5	.01010
10	.01	Mercury.....	.0349	34.6	.01009
11	.01	.....do.....	.0258	25.45	.01014
12	.01	.....do.....	.0451	44.55	.01013

NOTE.—Average factor for 0.1 N solution with silver is 0.1004, and with mercury, 0.1004. Average factor for 0.01 N solution with silver is 0.01017, and with mercury, 0.01012.

The writers have found that potassium thiocyanate solutions remain practically unchanged in composition for several months; evidently an occasional standardization is all that is necessary.

THE ESCHKA METHOD.

The method that is most widely used in metallurgical practice for determining mercury is based upon the heating of the sample in a crucible covered with a piece of gold or silver foil, on which the mercury is collected and subsequently weighed. Biewend [a] traces the history of this method as far back as 1836, but details were first published by Eschka [b] in 1872, and the method is variously known by his name or by the names of several modifiers of apparatus or procedure.

These modifications have taken the form of improvements in the construction of the cover or of the crucible and in the choice of reagents mixed with the ore. The modifications of apparatus have to do chiefly with the speed and convenience of assaying, but the numerous variations of reagent that have been proposed suggest that the method may possess inherent defects. Eschka used iron filings as the reagent, but under the reducing conditions thereby established, large proportions of sulphur or bituminous materials, such as not infrequently occur in mercury ores, tend to produce deposits on the cooled cover. Since oxidizing conditions are here obviously essential, the iron filings have been variously replaced by

[a] Biewend, H., Mittheilungen aus dem Probirlaboratorium; die trockene Quecksilberprobe: Berg.-Hüttenm. Ztg., Jahrg. 61, 1902, p. 441.

[b] Eschka, A., Beschreibung des Verfahrens zur Bestimmung des Quecksilbers in seinen Erzen: Oest. Ztschr. Berg.-Hüt., Jahrg 26, 1872, p. 67.

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Zdráhal [a] with minium, by Hausamann [b] with lead chromate, by Kroupa [c] with hammerscale (Fe_3O_4) and zinc oxide, and by Janda [d] with manganese dioxide and sodium carbonate. Kroupa, however, found it still necessary to make systematic corrections according to the richness of the ore. In general, low results were obtained, and the proportional error was greater with poor ores than with rich. A critical discussion of errors of the method is given by Castek.[e]

Two fairly well-known forms of apparatus for carrying out the Eschka method have been developed by Whitton [f] and James,[g] respectively, in this country. The writer's experience with the Whitton apparatus, using iron filings for admixture with the ore in accordance with his recommendation, confirms in the main the criticisms made by Castek. With ore containing more than a small per cent of sulphur or a trace of organic matter irregular results were obtained, frequently accompanied by a discoloration of the silver foil. As pointed out in the discussion of interfering elements (p. 19), certain types of mercurial materials require an oxidizing reagent for complete distillation of the mercury, whereas others require some substance like iron filings essentially reducing in its action. It is believed that the glass tube method of distillation possesses the necessary flexibility for dealing with these various types of material, as several different reagents can be used in successive layers and the opportunity for contact between the various vapors released by the sample and the reagents is much better than in any form of crucible.

With material carrying more than 15 per cent mercury there was a tendency for the results with the Whitton apparatus to be low, due, presumably, to the loss of mercury vapor. Occasionally with rich ores a few globules of mercury were found adhering to the upper part of the crucible, and there is danger, of course, that some of these may drop back into the charge and escape detection entirely.

ACKNOWLEDGMENT.

The writers desire to express their appreciation of the assistance rendered by W. C. Riddell, chemical engineer of the Bureau of Mines, in the early work that led to the development of the method described.

[a] Zdráhal, A., Die Eschka'sche Quecksilberprobe und ihre genauigkeit: Oest. Ztschr. Berg.-Hüt., Jahrg. 29, 1881, p. 485.

[b] Hausamann, Oscar, Zur Eschka'schen Quecksilberprobe: Oest. Ztschr. Berg.-Hüt., Jahrg. 29, 1881, p. 561.

[c] Kroupa, G., Ueber die genauigkeit der Quecksilberbestimmung nach A. Eschka: Berg.-Hüttenm., Jahrbd. k. k. Bergakad. Loeben und Pribram, 1889, p. 369.

[d] Janda, F., Die Ermittlung des Quecksilbers in schwefelantimon- und schwefelarsenhaltigen Quecksilberfahlerzen mittels der Golddeckelprobe: Oest. Ztschr. Berg.-Hüt., Jahrg. 47, 1899, p. 205.

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A BIBLIOGRAPHY ON ANALYTICAL METHODS FOR THE DETERMINATION OF MERCURY.

The following bibliography is believed to contain references to nearly all the important articles dealing with the determination of mercury published prior to October, 1919. Minor articles, concerned chiefly with the application of well-known methods to particular problems, have not in general been included. The more important fundamental papers are as follows: A. Eschka, 107; J. B. Hannay, 47; C. W. Hempel, 72, 84; M. J. Personne, 43; H. Rose, 101; E. Rupp, 68.

A number of the articles included in this bibliography are of interest to the metallurgist as well as to the analyst, particularly with reference to the possible hydrometallurgical treatment of quicksilver ores and products.

BIBLIOGRAPHY.

GRAVIMETRIC AND PRECIPITATION METHODS.

PRECIPITATION OF FREE MERCURY.

BY ZINC.

1. Jolles, Adolf. Über eine einfache und empfindliche Methode zum qualitativen und quantitativen Nachweis von Quecksilber im Harn: Monatsh. Chemie, Bd. 16, 1895, pp. 684–692.

   Hg in physiological solutions is first precipitated by Zn dust, the excess Zn dissolved, and the Hg amalgamated upon granulated Au.

   Schumacher, —, and Jung, W. 1900. (See No. 7.)

   Criticism of Jolles' method.

   Farup, P. 1900. (See No. 8.)

   Describes method for preliminary precipitation of Hg by Zn dust.

2. François, Maurice. Sur un nouveau procédé de dosage du mercure par le zinc et limaille: Compt. rend., t. 166, 1918, pp. 950–952.

   Hg is precipitated by Zn and the excess Zn dissolved in HCl. The Hg is readily obtained in a single globule.

BY COPPER.

3. Eschbaum, F. Ueber eine neue klinische Methode zur Bestimmung von Quecksilber im Harn. Deutsch. med. Wochenschr., vol. 26, 1900, p. 52.

   Hg present in physiological fluids is precipitated on Cu gauze spiral, distilled in a glass tube, and collected and weighed on Ag foil.

4. Richards, T. W., and Singer, S. K. Note on a method of determining small quantities of mercury: Journ. Am. Chem. Soc., vol. 26, 1904, p. 300–302.

   Hg is precipitated from nitrate solution by standing 6 to 7 hours in contact with Cu foil. A fresh piece of foil with 2 hours' standing completes the precipitation. Hg is determined by loss of weight of foil upon gentle ignition.

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4a. Elliott, J. A. New and delicate method for the detection of mercury: Journ. Am. Med. Assoc., vol. 68, 1917, pp. 1693–1694.

Copper dust is used as a precipitant in preference to wire or foil.

BY BRASS.

Fürbringer, P. 1878. (See No. 97).

BY STANNOUS CHLORIDE.

5. Rose, H. Handbuch der analytischen Chemie. Leipzig. 2d ed., 1839, vol. 2, pp. 169–172.

Reduction of Hg solution by $SnCl_2$, followed by collection and weighing of the free metal.

6. Namias, R. Determinazione volumetrica del mercurio: Gazz. Chim. ital., vol. 21, pt. 2, 1891, pp. 361–364.

Precipitation of Hg from either mercurous or mercuric solutions by $SnCl_2$, and titration of excess $SnCl_2$ by I.

7. Schumacher, —, and Jung, W. Eine einfache und zurvelässige Methode zur quantitativen Bestimmung des Quicksilbers im Harn: Ztschr. Anal. Chem., Jahrg. 39, 1900, p. 12–17. Arch. experim. Path. Pharm., Bd. 42, 1898, p. 138–148.

Criticism of Jolles' method (see No. 1), which does not remove all Hg. These authors prepare a gold-asbestos filter which collects the finely divided Hg precipitated by $SnCl_2$.

8. Farup, P. Über eine einfache und genaue Methode zur quantitativen Bestimmung von Quecksilber im Harn: Arch. experim. Path. Pharm., vol. 44, 1900, pp. 272–277. Chem. Zentralb., Jahrg. 1900, Bd. 2, pp. 213–214.

Determination of Hg in physiological substances by reduction with Zn dust, solution in HCl-$KClO_3$, reduction by $SnCl_2$ and collection on a gold-asbestos filter.

BY ALKALI ARSENITE.

9. Feit, W. Zur quantitativen Bestimmung des Thalliums und des Quecksilbers: Ztschr. anal. Chem., Jahrg. 28, 1889, pp. 318–322.

Hg in alkaline solution is reduced from mercuric state to metallic Hg by arsenious acid, followed by titration of excess arsenite with I.

10. Reichard, C. Die Maassanalytische Bestimmung des Quecksilbers durch arsenige Säure in alkalischer Lösung: Ztschr. anal. Chem., Jahrg. 37, 1898, pp. 749–751.

Hg is reduced from either mercuric or mercurous form to metallic Hg by arsenious acid in hot alkaline solution, followed by titration of excess arsenious acid with I or $KMnO_4$.

BY FORMALDEHYDE.

11. Rupp, E. Ueber die massanalytische Bestimmung des Quecksilbers nach rhodantitrimetrischem, jodometrischem, und acidimetrischem Verfahren, Arch. Pharm., Bd. 243, 1905, pp. 300–303: Ueber die columetrische Bestimmung des Quecksilbers: Ber. Deutsch. chem. Gesell., Jahrg. 39, 1906, p. 3702–3704; Notiz zur jodometrischen Bestimmung des Quecksilbers: Ber. Deutsch. chem. Gesell., Jahrg. 40, 1907, p. 3276; Chem. Ztg., vol. 32, 1908, p. 1077.

An alkaline solution of K_2HgI_4 is reduced to free Hg by CH_2O, shaking 1 to 2 minutes for complete reduction. The determination is completed volumetrically. (See also No. 74 and No. 84.)

12. Smith, C. E. Volumetric determination of mercury: Am. Jour. Pharm., vol. 83, 1911, pp. 311–15; Chem. News, vol. 105, 1912, p. 14.

In reference to Rupp's iodine method (See No. 11), varying alkalinity during reduction leads to divergent results. Standard strength of NaOH is prescribed. Also in using Hempel's method (See No. 70) HgCl dissolves rapidly if I is added *before* KI.

BY CHLORAL HYDRATE.

13. Brown, L. A. A rapid volumetric method for estimating mercury: Merck's Report, vol. 17, 1908, pp. 57–58.

Hg is precipitated as such by chloral hydrate in alkaline solution, separated and dissolved in HNO_3. Completed volumetrically. (See No. 73.)

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BY HYDRAZINE OR HYDROXYLAMINE.

14. KNOEVENAGLE, E., and EBLER, E. Ueber die Anwendbarkeit der Hydroxylamin und Hydrazin-Salze in der qualitativen Analyse: Ber. Deut. chem. Gesell., Jahrg. 35, 1902, p. 3055–3067.

Hg is quantitatively precipitated by NH_2OH or N_2H_4 from alkaline solutions, and slowly but completely precipitated by N_2H_4 from weak acetic acid solutions.

15. DUCCINI, C. Su un nuovo metodo di determinazioni quantitative del mercurio allo stato metallico: Gazz. Chim. ital., vol. 43, pt. 2, 1913, pp. 693–699.

Hg is reduced in alkaline solution to free Hg by N_2H_4; the Hg is collected on a tared filter and weighed, or the nitrogen liberated may be measured by method described by Purgotti-Rimini (Gazz. Chim. ital., vol. 34, pt. 1, p. 224.)

EBLER, E. 1905. (See No. 82.)
STÜWE, W. 1914. (See No. 83.)

PRECIPITATION OF CALOMEL.

BY ORGANIC REAGENTS.

16. VON BONSDORFF, P. A. Ueber die Scheidung von Quecksilber und Kupfer mittelst Ameisensaure: Pogg. Ann., Bd. 33, 1834, pp. 73–80.

Hg is precipitated as HgCl by $HCHO_2$ in a slightly alkaline solution.

ROSE, H. 1860. (See No. 19.)

Adverse criticism of precipitation by formates.

17. HAGER, H. Eine neue Methode zur gewichtsanalytischen Bestimmung der glycose und des Quecksilbers: Pharm. C.-H., vol. 18, 1877, p. 313; Ztschr. anal. Chem., Jahrg. 17, 1878, p. 380.

$HgCl_2$ is reduced to HgCl by glucose, and is then weighed on tared filter.

18. RIESSER, O. (Production and excretion of formic acid; estimation of formic acid in pure solutions and in urine, together with a new method for the titration of calomel.) Ztschr. Physiol. Chem., Bd. 96, 1916, pp. 355–366; Jour. Chem. Soc. London, vol. 110, pt. 2, p. 455.

In determination of HCHO, HgCl is formed and this is titrated without filtering by adding KI and I solution and titrating excess I. The method of titration is indistinguishable from Hempel's method. (See No. 72.)

BY FERROUS SULPHATE AND ALKALI.

HEMPEL, C. W. 1858. (See No. 84.)
HASWELL, A. E. 1882. (See No. 57.)
VON JÜPTNER, HANS. 1882. (See No. 58.)

BY PHOSPHOROUS ACID.

19. ROSE, H. Ueber die quantitative Bestimmung des Quecksilbers und über die Trennung desselben von andern Metallen: Pogg. Ann., Bd. 110, 1860, pp. 529–546.

Discusses precipitation of HgCl by phosphorous acid or by alkaline formates. The former is approved and the latter rejected as incomplete.

20. VANINO, L., and TREUBERT, F. Zur quantitativen Bestimmung der Quecksilberoxydsalze: Ber. Deut. chem. Gesell., Jahrg. 30, 1897, pp. 1999–2001, 2808–2809.

The precipitation of HgCl by H_3PO_3 is greatly accelerated by presence of H_2O_2, and precipitation may take place in hot solutions to advantage. Dilute HNO_3 and chlorine water resembles H_2O_2 in action, but are not so applicable to analysis.

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BY STANNOUS CHLORIDE.

21. LABORDE, J. Sur un procédé de dosage volumetrique du mercure: Jour. Pharm. Chim., ser. 5, t. 29, 1892, pp. 507–509; Chem. Zentralb., 1893, Bd. 2, p. 156.

Titration of $HgCl_2$ by $SnCl_2$ to first appearance of metallic Hg.

BY SULPHUR DIOXIDE.

VITALI, D. 1894. (See No. 63.)

BY HYDROGEN PEROXIDE AND AMMONIUM TARTRATE.

22. KOLB, A., and FELDHOFEN, A. Bestimmung des Quecksilbers durch Reduktion des Quecksilberchlorids zu Chlorür mit Wasserstoffperoxyd: Ztschr. angw. Chem. Jahrg. 20, 1907, pp. 1977–1980.

$HgCl_2$ is reduced to HgCl by H_2O_2 in slightly acid solution of ammonium tartrate. HgCl is filtered off and weighed on the paper or titrated with I. (Rupp's method. See No. 76.) Pb and Cu interfere with the analysis.

BY SODIUM CHLORIDE.

ODDO, BERNADO. 1909. (See No. 55.)

PRECIPITATION OF MERCURIC SULPHIDE.

23. LOWE, JULIUS. Ueber die quantitative Bestimmung des Silbers, Bleis, Quecksilbers, Wismuths, und Cadmiums in Form von Schwefelmetallen: Journ. Prakt. Chemie, Bd. 77, 1859, pp. 73–79.

Precipitated HgS is cleansed of free S by boiling with Na_2SO_3.

KROUPA, G. 1889. (See No. 111.)

24. VOLHARD, J. Ueber krystallisirtes Quecksilberoxychlorid und die Bestimmung des Quecksilbers: Ann. der Chemie, Bd. 255, 1889, pp. 252–256.

A standard method. Hg is obtained in alkaline sulphide solution and is precipitated by boiling with NH_4OH, which neutralizes the excess alkali.

25. FAKTOR, F. J. Ueber die Einwirkung des Natriumthiosulfats auf einige Metallsalze und seine Anwendung in der quantitativen Analyse: Ztschr. anal. Chem. Jahrg. 39, 1900, pp. 345–354.

Hg is precipitated by $Na_2S_2O_3$. The precipitate contains free S, and is therefore dissolved, and the mercury determined electrically.

26. WEGELIUS, HENRIK, and KILPI, SULO. Eine Methode der Quecksilberbestimmung in jodhaltigen Lösungen: Ztschr. anorg. Chem., Bd. 61, 1909, pp. 413–416.

The determination of Hg in KI solutions with AgCl, filtering off the AgI formed, and precipitating HgS from the filtrate. (Quantitative results were not obtained by precipitating HgS from the I solution.

27. MCBRIDE, R. S. Equilibrium in the system, mercuric chloride-pyridine: Jour. Phys. Chem., vol. 14, 1910, p. 189.

Compares the method of precipitating Hg as HgS with an electrolytic method.

28. FRANK, F., and BIRKNER, K. Zur Bestimmung von Zinnober und Goldschwefel in Kautschukwaren: Chem. Ztg., Jahrg. 34, 1910, pp. 49–50.

Describes method for determination of cinnabar in rubber. Hg is separated and weighed as sulphide.

PROCTER, H. R., and SEYMOUR-JONES, A. 1911. (See No. 92.)

Formic or citric acids retard precipitation of HgS.

29. CASTAÑARES, A. P. A new method for the analytical and quantitative separation of mercury from bismuth: 8th Internat. Cong. Appl. Chem., vol. 25, 1912, pp. 39–40.

In presence of much nitrate ion, mercuric salts are not precipitated by ammonium carbonate. After separation of Bi, HgS is precipitated, free from S, by $(NH_4)_2S$.

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PRECIPITATION OF MERCURIC IODIDE.

PERSONNE, M. J. 1863. (See No. 43.)

EVESQUE, E., and LAHACHE, J. E. 1895. (See No. 45.)

30. LIVERSEDGE, S. G. A rapid method for the estimation of mercuric salts in aqueous solution: Analyst, vol. 33, 1908, pp. 217–219.

HgI_2 is precipitated by KI in presence of H_3PO_4, which lessens the solvent action of a slight excess of KI, and is extracted by ether; the ether is then distilled and the HgI_2 weighed. Method is not highly accurate.

31. RUPP, E., and LEHMANN, F. Ueber eine acidimetrische Gehaltsbestimmung der weissen Quecksilber-Präcipitate: Pharm. Ztg., vol. 52, 1907, p. 1014.

Gives method for determining Hg in ammoniated compounds, based on the reaction—

$$NH_2HgCl + 2\,KI + 2\,H_2O = HgI_2 + KCl + NH_4OH + KOH.$$

The alkali produced is titrated with HCl.

PRECIPITATION OF AMMONIUM DERIVATIVES.

HANNAY, J. B. 1873. (See No. 47.)
TUSON, R. V., and NEISON, EDMUND. 1877. (See No. 48.)
JONES, CHAPMAN. 1892. (See No. 49.)
BRESSANIN, G. 1910. (See No. 71.)
CASTAÑARES, A. P. 1912. (See No. 29.)

Mercuric ion is not precipitated by ammonium carbonate in presence of much nitrate ion.

OTHER PRECIPITATES.

32. DE MARIGNAC, C. Memoir sur la composition et les formes cristalline des nitrates de protoxyde de mercure: Ann. Chem. Phys., ser. 3, t. 27, 1849, pp. 315–333. Jahresber. v. Liebig u. Kopp., 1849, p. 594.

Mercury nitrates or nitrites may be ignited to HgO and thus weighed. Method has very limited application.

LIEBIG, JUSTUS. 1853. (See No. 54.)

Sodium phosphate precipitates mercuric salts from the nitrate but not from the chloride.

33. VOHL, H. Beiträge zur quantitativen chemischen Analyse: Ann. der Chemie, Bd. 94, 1855, pp. 220–222.

Chloride solution containing Hg is repeatedly evaporated on the water bath with H_2SO_4; all chlorine except that associated with Hg is thus expelled. This Cl is finally determined by precipitation with $AgNO_3$.

34. SCHERER, J. J. Lerhbuch der Chemie, Bd. 1, 1861, p. 513.

From mercuric nitrate or chloride, $Na_2S_2O_3$ precipitates $2HgS.Hg(NO_3)_2$ or $2\,HgS.HgCl_2$. Scherer titrates with $Na_2S_2O_3$ in very dilute solution until precipitate ceases to form.

35. RENK, —. Untersuchungen über das Verstäuben und Verdampfen von Quecksilber mit besonderer Berücksichtigung der Verhältnisse in Spiegelbeleg-Anstalten: Arb. aus dem Kaiserl. Gesundheitsamt, Bd. 5, 1889, pp. 113–138. Mentioned by L. Grünhut in Specielle Analytische Methoden: Ztschr. anal. Chem., Jahrg. 36, 1897, p. 337. (See No. 36 for abstract.)

36. HILGER, A., and v. RAUMER, E. Ueber den Quecksilbergehalt der Luft in Spiegelbeleg-Anstalten: Forsch.-Ber. ü. Lebensmittel, Jahrg. 1, 1894, pp. 32–37. Mentioned by L. Grünhut in Specielle Analytische Methoden: Zitschr. anal. Chem., Jahrg. 36, 1897, p. 338.

For determination of mercury in air the latter is drawn through an asbestos filter and over gold foil in a weighted tube.

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37. Cazeneuve, P. Sur la disphenylcarbazide, réactif très sensible de quelques composés métalliques: Cuivre, mercure, fer au maximum, acide chromique: Bull. Soc. chim. France, sér. 3, t. 23, 1900, p. 701.

Diphenylcarbazone with mercurous or mercuric salts gives a deep blue color or precipitate A delicate qualitative test. Further developed by Böttger. (See No. 42.)

38. Peters, C. A. The separation and determination of mercury as mercurious oxalate: Am. Jour. Sci., vol. 9, ser. 4, 1900, pp. 401–406.

Mercury is precipitated as oxalate, and the precipitate dried over H_2SO_4 and weighed, or excess oxalate is titrated by $KMnO_4$. Small amounts of mercuric salts do not interfere.

39. Pretzfeld, C. J. The gravimetric determination of mercury and its separation from arsenic, antimony, and copper: Jour. Am. Chem. Soc., vol. 25, 1903, pp. 198–209.

Hg is precipitated and weighed as the arsenate. The methods of Vanino and Treubert (See No. 20) and of Faktor (See No. 25) are discussed.

Rupp, E., and Krauss, L. 1903. (See No. 75.)

Hg is precipitated as $Hg(IO_3)_2$.

40. Litterscheid, F. M. Ueber eine gewichts-und maassanalytische Bestimmungsmethode des Quecksilbers: Arch. Pharm., Bd. 241, 1903, p. 306; Ztschr. anal. Chem., Jahrg. 46, 1907, p. 443.

Hg is precipitated as $(NHg_2)_2CrO_4 \cdot 2H_2O$ by $K_2Cr_2O_7$ and NH_4OH. Excess chromate may be determined iodometrically, but weighing the precipitate is preferred.

41. Robertson, P. W. A volumetric method for estimating mercury: Chem News, vol. 95, 1907, pp. 253–254.

Describes method for precipitating the double salt $ZnHg(SCN)_4$, from HNO_3 solution by excess NH_4SCN and $ZnSO_4$. The determination is completed volumetrically, by adding $AgNO_3$ and titrating the excess NH_4SCN.

Jamieson, G. S. 1919. (See No. 59a.)

42. Böttger, W. Bestimmung kleiner Mengen Quecksilbersalz in starker Verdünnung: Chem. Ztg., Jahrg. 39, 1915, p. 817.

For the determination of minute amounts of Hg in solution, the mercury is precipitated as mercuric diphenyl-carbazide for separation. This compound is decomposed by Carius' method (heating with HNO_3 in sealed tube) and the Hg is deposited by electrolysis on a Au wire. Or the mercuric diphenyl-carbazide may be determined by a spectral-photometric method using the Hg arc (44–546).

VOLUMETRIC METHODS.

DIRECT TITRATIONS.

WITH POTASSIUM IODIDE.

43. Personne, M. J. Mémoire sur le dosage du mercure par les volumes à l'aide de liqueurs titrées: Compt. rend., t. 56, 1863, pp. 951–954; Bull. Soc. chim. France, 1863, p. 274; Jour. Pharm. chim., t. 43, 1863, p. 477; abstracted in Ztschr. anal. Chem., Jahrg. 1863, p. 381.

The mercury is dissolved by heating in a NaOH solution while passing in chlorine gas. The excess chlorine is boiled out ($HgCl_2$ does not volatilize from hot alkaline solution) and the solution, made up to known volume, is used to titrate a known amount of KI in solution. The appearance of a permanent HgI_2 precipitate marks the end point.

44. Carnot, Adolphe. Sur un nouveau procédé de dosage volumétrique de l'argent, du mercure et du thallium, au moyen de l'iodure de potassium: Compt. rend., t. 109, 1889, p. 177.

Hg in HNO_3 solution containing starch is titrated with KI. As soon as all Hg is precipitated as HgI_2, I is liberated by the HNO_3.

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45. EVESQUE, E., and LAHACHE, J. E. Note sur le dosage de mercure dans le papier au sublime des approvisionnemente du service de ante: Arch. de Méd. et de Pharm. milit., vol. 26, 1895, pp. 59–61; Apoth. Ztg., vol. 10, 1895, p. 590.

Describes method used for certain pharmaceutical preparations. Employs titration of known KI solution containing $MgSO_4$ (to prevent dissociation of precipitate) by the mercuric solution to permanent red precipitation. The reactions are as follows:

$$4KI - Hg(NO_3)_2 = K_2HgI_4 - 2KNO_3.$$

$$K_2HgI_4 - Hg(NO_3)_2 = 2HgI_2 - 2KNO_3 \text{ (end-point reaction).}$$

Is a modification of Personne's method. (See No. 42.)

46. SEAMON, W. H. A volumetric method for the determination of mercury: Eng. and Min. Jour., vol. 87, May, 1909, p. 1047.

Titrates mercury solution with KI in the presence of a little nitrous acid. External starch indicator is used. When all Hg is precipitated as HgI_2 the nitrous acid reacts to form free iodine.

WITH POTASSIUM CYANIDE.

47. HANNAY, J. B. On new processes for mercury estimation, with some observations on mercury salts: Jour. Chem. Soc. London, vol. 26, 1873, pp. 565–574.

A mercuric solution made slightly turbid by NH_4OH is titrated with KCN to disappearance of turbidity (ammonia gives no precipitate in mercuric cyanide solutions). Volatility of mercury chlorides and cyanides from solution is discussed. A solubility curve of $HgCl_2$ is given.

48. TUSON, R. V., and NEISON, EDMUND. On the volumetric estimation of mercury: Jour. Chem. Soc. London, vol. 32, 1877, pp. 679–686.

Gives results of investigation of Hannay's cyanide method, confirming its accuracy. Some recommendations are made as to technicque.

49. JONES, CHAPMAN. The volumetric estimation of mercury: Jour. Chem. Soc. London, vol. 61, 1892, pp. 365–367.

Criticises Hannay's cyanide method, Tuson and Neison's modifications, on ground of indefiniteness of end point. A more tedious technicque is given with the claim that results are then accurate.

50. MORAWITZ, H. Volumetrische Bestimmung von Mercurisalzen: Ztschr. anorg. Chem., Bd. 60, 1908, pp. 456–458.

Discusses Rupp's cyanide acidimetric method. (See No. 68.) Morawitz titrates directly with KCN, using p-nitrophenol as indicator. In Ztschr. anorg. Chem., Bd. 62, 1909, is found a controversy concerning the chemistry and originality of this method, between L. W. Andrews. (pp. 171–172) and Morawitz (pp. 310–312).

WITH POTASSIUM THIOCYANATE.

51. VOLHARD, J. Die Anwendung des Schwefelcyanammoniums in der Maassanalyse: Ann. der Chemie, Bd. 190, 1878, pp. 1–61.

Classical paper on titration of Ag or of halides by means of thiocyanate. The titration of Hg by potassium thiocyanate in a dilute and almost neutral solution is here first proposed as a method of no great accuracy.

52. RUPP, E., and KRAUSS, L. Ueber die maassanalytische Bestimmung von Quecksilber, sowie Quecksilber und Silber: Ber. Deut. chem. Gesell., Jahrg. 35, 1902, pp. 2015–2017.

Hg may be directly titrated by thiocyanates if HNO_3 is present in considerable excess.

53. KNOX, JOSEPH. The volumetric estimation of mercury and the estimation of silver in the presence of mercury: Jour. Chem. Soc. London, vol. 95, 1909, pp. 1768–72.

Finds that Rupp's potassium thiocyanate method is accurate if all Hg is in mercuric state, but that on dissolving HgO in HNO_3 small amounts of mercurous salts are always formed.

WITH STANNOUS CHLORIDE.

LABORDE, J. 1893. (See No. 21.)

Titrates $HgCl_2$ with $SnCl_2$ to first appearance of metallic Hg.

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WITH SODIUM CHLORIDE.

54. LIEBIG, JUSTUS. Ueber einige Harnstoffverbindung und eine neue Methode zur Bestimmung von Kochsalz und Harnstoff im Harn: Ann. der Chemie, Bd. 85, 1853, p. 307.

Titrates freshly precipitated mercuric phosphate by adding NaCl until the precipitate redissolves.

55. ODDO, BERNARDO. L' impiego della difenilcarbazide simmetrica in analisi volumetrica; dossagio del mercurio nei suoi sali al minimo: Gazz. Chim. ital., vol. 39, pt. 1, 1909, pp. 666–671.

Gives method for titration of $HgNO_3$ by NaCl, using as an external indicator sym.-dipenylcarbazide, which gives a blue color with $HgNO_3$.

56. VOTOCEK, E. (Volumetric determination of chlorine, bromine, cyanogen, and mercuric ions.) Chem. Ztg., Jahrg. 42, 1918, pp. 257–260 and 271–272.

Titrates mercuric sulphate solution by first adding sodium nitroprusside and HNO_3 to form a white precipitate and titrating with NaCl to produce a clear solution.

56a. VOTOCEK, E., and PAZOUREK, J. (Gravimetric determination of copper by means of sodium nitroprusside and the separation of copper from mercury): Chem. Ztg., Jahrg., 1919, p. 939.

Copper is precipitated by nitroprusside while Hg is held in solution by excess NaCl by standard Hg solution.

WITH SODIUM THIOSULPHATE.

SCHERER, J. J. 1861. (See No. 34.)

Gives a precipitation method of titration. Technique is fully described.

WITH POTASSIUM PERMANGANATE.

57. HASWELL, A. E. Volumetrische Bestimmung des Quecksilbers mit Kaliumpermanganat: Repertorium der anal. Chem., Bd. 2, 1882, pp. 84–87.

$HgCl_2$ is reduced to HgCl by $FeSO_4$ in alkaline solution. The solution is acidified and excess ferrous iron oxidized by just enough $KMnO_4$. In presence of $SnCl_4$ as catalyzer the HgCl is now rapidly oxidized by the ferric iron, and the equivalent of ferrous iron produced is titrated by $KMnO_4$. (Compare Hempel, No. 84.)

58. VON JÜPTNER, HANS. Volumetrische Bestimmung des Quecksilbers mit Kaliumpermanganat: Oest. Ztschr. Berg. Hüt., Jahrg. 30, 1882, pp. 287–288.

Describes Haswell's method, with more expanded treatment of the reactions involved.

WITH POTASSIUM IODATE.

59. JAMIESON, G. S. A new volumetric method for the determination of mercury: Am. Jour. Sci., vol. 33, ser. 4, 1912, pp. 349–351.

Titration of HgCl by adding KIO_3 solution in presence of $CHCl_3$ and much HCl. End point is shown by the disappearance of the violet iodine color from the $CHCl_3$ solution. Reaction is as follows:

$$4HgCl+KIO_3+6HCl=4HgCl_2+KCl+ICl+3H_2O$$

59a. ————. The gravimetric and volumetric determination of mercury precipitated as mercury zinc thiocyanate: Jour. Ind. Eng. Chem., vol. 11, 1919, pp. 296–297.

WITH AMMONIA.

60. ARCHETTI, A. Ueber die Einwirkung von Natriumhyposulfit von korrosive sublimat: Boll. chim. farm., vol. 39, 1900, p. 765.

(See No. 61 for abstract.)

61. UTZ, F. Volumetrische Bestimmung löslicher Quecksilberverbindungen, besonders des Sublimats: Pharm. C.-H., vol. 42, 1901, pp. 81–82.

Based on the reaction—

$$HgCl_2+2NH_4OH=NH_2HgCl+NH_4Cl+2H_2O.$$

Titration by ammonia in presence of phenolphthalein gives a red color at the end point. (Compare Bressanin, No. 71.)

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INDIRECT AND RESIDUAL TITRATIONS.

ACIDIMETRIC.

62. KROUPA, GUSTAV. Beitrag zur volumetrischen Quecksilberbestimmung: Oest. Ztschr. Berg.-Hüt., Jahrg. 31, 1883, p. 604.

Hg is precipitated as HgCl and the HgCl decomposed by H_2S. The HCl formed is titrated by Mohr's $AgNO_3$ method (K_2CrO_4 indicator).

63. VITALI, D. ————: Boll. chim. farm., 1894, p. 365. Described by L. P. Andrews (Am. Chem. Jour., vol. 30, 1903, p. 192).

To a neutral $HgCl_2$ solution excess SO_2 is added, the excess boiled out, and the liberated acids titrated. The reaction is—

$$2HgCl_2+SO_2+2H_2O=2HgCl+H_2SO_4+2HCl.$$

64. ANDREWS, L. W. The volumetric determination of mercury and of hydrocyanic acid: Am. Chem. Jour., vol. 30, 1903, pp. 187–193.

Gives an acidimetric method depending on the nondissociation of $Hg(CN)_2$. The reaction is as follows:

$$HgCl_2+2HCN=Hg(CN)_2+2HCl.$$

The titration is with KOH, nitrophenol being used as an indicator.

ALKALIMETRIC.

65. LESCOEUR, H. Sur le dosage alcalimétrique des métaux; dosage du mercure: Bull. Soc. chim. France, ser. 3, t. 17, 1897, pp. 706–712.

Titrates mercuric and mercurous solutions directly with alkaline hydroxides. Phenolphthalein and helianthin are used as indicators.

66. RIMINI, ENRICO. Sul dosaggio dell' idrazina e di alcuni suoi derivati: Atti della Reale Accad. dei Linceid, ser. 5, vol. 12, pt. 2, 1903, pp. 376–381, ser. 5, Sul dosaggio idiometrico dei sali d'idrazina e sul loro impiego nelle analisi volumetriche, vol. 15, pt. 2, 1906, pp. 320–325.

Based on the reaction—

$$N_2H_4.H_2SO_4+2HgCl_2+5NaOH=4NaCl+NaHSO_4+2Hg+N_2+5H_2O.$$

The excess NaOH is titrated.

67. GOY, S. Ueber eine einfache acidmetrische Bestimmung des Quecksilbercyanids: Apoth. Ztg., vol. 22, 1907, pp. 532–533.

Hg present in a neutral solution of cyanides is determined by adding excess KI and titrating with HCl (methyl orange indicator). Reaction is—

$$Hg(CN)_2+4KI=K_2HgI_4+2KCN.$$

KCN, by hydrolysis, gives KOH.

68. RUPP, E. Ueber die maassanalitische Bestimmung des Quecksilbers nach rhodantimetrischen, jodometrischen und acidimetrischen Verfahren: Chem. Ztg., Jahrg. 32, 1908, pp. 1077–1079.

An excess of standard KCN solution is added to the neutral mercuric cyanide. The excess KCN hydrolyses, giving KOH which is titrated by HCl.

70. ANDREWS, L. W. Ueber die maassanalytische Bestimmung des Quecksilbers nach acidimetrischen Verfahren: Chem. Ztg., Jahrg. 33, 1909, p. 157.

Recommends p-nitrophenol as indicator in Rupp's KCN-HCl titration. (See No. 68.)

71. BRESSANIN, G. Volumetrische Bestimmung des Quecksilbers mittels Ammoniaks: Ann. Chim. anal., t. 15, 1910, pp. 413–415.

Gives method for certain pharmaceutical preparations of $HgCl_2$. NH_2HgCl, is precipitated with excess ammonia and the excess titrated with HCl. Conditions must be closely regulated to prevent formation of other compounds of Hg. (Compare No. 61.)

IODIMETRIC.

72. HEMPEL, C. W. Allgemein anwendbare volumetrische Bestimmungsmethode des Quecksilbers: Ann. der Chemie, Bd. 110, 1859, pp. 176–181.

Titrates HgCl by adding KI and standard iodine solution and titrating excess iodine. (See Smith, No. 12.) The reaction is as follows:

$$2HgCl+I_2+6KI=2K_2HgI_4+2KCl.$$

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FEIT, W. 1889. (See No. 9.)

NAMIAS, R. 1891. (See No. 6.)

REICHARD, C. 1898. (See No. 10.)

73. NORTON, J. T., JR. The titration of mercury by sodium thiosulphate: Am. Jour. Sci., ser. 4, vol. 10, 1900, pp. 48–54.

Describes method of determining mercury by precipitation of Hg with $Na_2S_2O_3$ and titration of excess reagent with I. Is applicable only within a rather narrow range of conditions.

74. RUPP, E. Eine maassanalytische Bestimmungsmethode des Quecksilberchlorids: Arch. Pharm., Bd. 238, 1900, p. 298.

$HgCl_2$ solution is reduced by Fe powder, filtered, all Fe in the filtrate oxidized by $KMnO_4$, and the ferric iron determined iodimetrically.

75. RUPP, E., and KRAUSS, L. Ueber Metallitration mittels Jodsäure: Arch. Pharm., Bd. 241, 1903, p. 438.

Describes method for determination of $Hg(NO_3)_2$ or $HgSO_4$ by precipitating with KIO_3 and titrating excess KIO_3 with I.

RUPP, E. 1905. (See No. 11.)

Formaldehyde solution containing free Hg is acidified with acetic acid, the Hg oxidized by iodine to K_2HgI_4, and the excess I titrated.

76. MULLER, J. A. Sur le dosage volumétrique du mercure dans ses minerais Bull. Soc. chim. France, sér. 4, t. 1, 1907, pp. 1169–1173. (See No. 11.)

A report on tests of Rupp's iodine method with known Hg solutions. Good results are obtained with N/10 solutions.

77. RUPP, E., and LEHMANN, F. Zur Gehaltsbestimmung von Unguentem Hydragyr cinereum: Apoth. Ztg., Bd. 23, 1908, pp. 590–591; 1918, p. 590.

An application of Rupp's iodine method to analysis of mercuric cyanide. (See No. 11.)

78. UTZ, F. ————: Zentralb. Chem. Pharm., 1908, p. 483.

States that in a comparison of many methods of determining $HgCl_2$, Rupp's iodine method (See No. 11) proved best.

79. RUPP, E., and LEHMANN, F. Ueber die titrimetrische Trennung von Quecksilber und Silber: Chem. Ztg., Jahrg. 34, 1910, pp. 229–230.

States that Rupp's iodine method for Hg is applicable in the presence of Ag, as shown by experiment. (See No. 11.)

80. GRÜTER, R. Zur Maassanalytischem Bestimmung des Quecksilbers in galenischen Praparaten: Pharm. Ztg., vol. 55, 1910, pp. 427–428.

Rupp's iodine method applied to galenical preparations. Detailed directions are given, (See No. 11.)

81. REINTHALER, F. Ueber die auf Reduktion zu Metall beruhenden volumetrischen Quecksilberbestimmungsmethoden: Chem. Ztg., Jahrg. 35, 1911, pp. 593–595.

Shows that in Rupp's iodine method, two sources of error are the tendency of CH_2O to form a condensation product with starch, masking the end point, and the tendency of, CH_2O to reduce K_2HgI_4. (See No. 11.)

SMITH, C. E. 1911. (See No. 12.)

In using Hempel's titration for HgCl, if the I is added first and then followed by the KI, solution is quickly effected.

RIESSER, O. 1916. (See No. 18.)

82. EBLER, E. Die gasometrische und titrimetrische Bestimmung des Quecksilbers durch Hydrazinsalze, und die gasometrische Bestimmung des Hydrazins durch Quecksilbersalze: Ztschr. anorg. Chem., Bd. 47, 1905, pp. 377–385. (See No. 83.)

83. STÜWE, W. Maassanalytische Bestimmung des Quecksilberchlorids: Chem. Ztg. Jahrg. 35, 1914, pp. 145–154.

$HgCl_2$ is reduced by N_2H_4; the excess N_2H_4 is oxidized by I, and the excess I titrated. Based on the reactions—

$$2HgCl_2+N_2H_4=2Hg+N_2+4HCl$$
$$2I_2+N_2H_4=N_2+4HI$$

The two authors differ in details of procedure.

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BY PERMANGANATE.

84. HEMPEL, C. W. Neue volumetrische Methode der Bestimmung des Quecksilbers: Ann. der Chemie, Bd. 107, 1858, pp. 98–100.

Hg is obtained in chloride solution free from nitrates; reduced to mercurous form by excess standard $FeSO_4$ in alkaline solution; acidified, and HgCl filtered off. The excess of ferrous iron is titrated by $KMnO_4$.

PETERS, C. A. 1900. (See No. 38.)

85. RANDALL, D. L. The titration of mercurous salts with potassium permanganate: Am. Jour. Sci., vol. 23, ser. 4, 1907, pp. 137–140.

Mercurous salts in nitrate or sulphate solutions are oxidized by $KMnO_4$, excess of $FeSO_4$ added, and the titration completed with $KMnO_4$. Up to 3 per cent free HNO_3 may be present.

BY CYANIDE.

86. DENIGÈS, G. Méthode générale pour le dosage du mercure sous une forme quelconque: Bull. Soc. chim. France, sér. 3, t. 15, 1896, pp. 862–871.

Describes a modification of Hannay's cyanide method, consisting of adding KCN in excess and titrating the excess with $AgNO_3$ in the presence of iodide as an indicator. States that table of corrections is necessary for accurate work.

BY THIOCYANATE.

87. COHN, R. Eine neue Methode zur maass- und-gewichts-analytischen Bestimmung von Quecksilber, Kupfer, und Zinc: Ber. Deut. chem. Gesell., Jahrg. 34, 1901, pp. 3502–3508.

Titrates $Hg(NO_3)_2$ solutions with thiocyanates, the solution being made weakly acid with HNO_3. Is a residual titration, $AgNO_3$ being used as the intermediate.

ROBERTSON, P. W. 1907. (See No. 41.)

BY CHLORIDE.

88. MOHR, C. F. Lehrbuch der Titriermethode. 3d ed., 1868, p. 395.

Mercurous salts are precipitated by adding NaCl and the excess chloride is titrated by adding $AgNO_3$, with chromate as the indicator.

COLORIMETRIC METHODS.[a]

AS MERCURIC SULPHIDE.

89. VIGNON, LÉO. Dosage du mercure dans les solutions étendues de sublimé. Compt. rend., t. 116, 1893, pp. 584–586.

Describes a colorimetric method for determining Hg as HgS in very dilute solutions.

90. SCHUMACHER, —, and JUNG, W. Eine klinische Methode zur Quecksilberbestimmung im Harn: Ztschr. anal. Chem., Jahrg. 41, 1902, p. 461.

Determines Hg in physiological solutions by a colorimetric H_2S method.

91. HEINZELMANN, A. Zur colorimetrischen Bestimmung des Quecksilbers im Harn: Chem. Ztg., Jahrg. 35, 1911, p. 721.

Describes a colorimetric H_2S method for determining Hg in physiological fluids. Preliminary precipitation is by zinc.

92. PROCTER H. R., and SEYMOUR-JONES, R. A. The estimation of soluble mercuric salts at great dilution: Jour. Soc. Chem. Ind., vol. 30, 1911, pp. 404–405.

States that in applying the colorimetric H_2S method, the presence of formic or citric acids prevents the precipitation of HgS, forming colloidal solutions.

AS MERCURIC DIPHENYL CARBAZIDE.

CAZENEUVE, P. 1900. (See No. 37.)

93. MÉNIÈRE, P. Nouvelle méthode de dosage de la vapeur de mercure dans l'air: Compt. rend., t. 146, 1908, pp. 754–756.

Describes a colorimetric method of determining Hg in air, based on the blue color of mercuric diphenyl carbazide (a color chart accompanies the paper).

BÖTTGER, W. 1915. (See No. 42).

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[a] See direct titrations, p. 29.

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DISTILLATION METHODS.

DISTILLATION IN A TUBE NOT SEALED AT EITHER END.

94. ERDMANN, O. L., and MARCHAND, R. F. Ueber die Atomgewichte des Kupfers, des Quecksilbers, und des Schwefels: Jour. prakt. Chemie, Bd. 31, 1844, pp. 385–402.

States that in determining the atomic weight of mercury, the mercury was distilled from its compounds in a current of CO_2 and condensed on gold leaf.

95. WANDESLEBEN, —. Die quantitative Bestimmung des Quecksilbers: Jour. prakt. Pharm., Bd. 24, 1852, p. 385.

Hg compounds are heated with CaO or soda-lime in a H_2 gas stream. The Hg is condensed in a glass bulb.

96. KÖNIG, C. R. Analyse eines technisch angewandten Kupfersmalgams: Jour. prakt. Chemie, Bd. 70, 1857, p. 64.

Hg content of amalgams may be determined by distilling out the Hg and collecting on Au leaf. (See Erdmann and Marchand, No. 94.)

97. NEUBAUER, C. Auf Physiologie und Pathologie bezügliche Methoden; Quecksilbernachweis im Harn mittelst Messingwolle: Ztschr. anal. Chem., Jahrg. 17, 1878, p. 526.

Review of article by P. Fürbringer (Berliner klin. Wochenschrift, 1878, M. 23) describing a qualitative test.

98. JANNASCH, P., and LEHNERT, H. Ueber die Bestimmung des Schwefels in unorganischen Sulphiden durch Glühen derselben in einem Sauerstoffstrom und Auffangen der flüchtigen Oxyde in Wasserstoffsuperoxyd: Ztschr. anorg. Chem., Bd. 12, 1896, pp. 129–131 and 132–133.

Is one of a series of articles treating of the distillation of metallic sulphides in an oxygen stream. The sulphur is completely eliminated, and, in cinnabar, the mercury is distilled in the metallic state.

99. ABELMAN, ARTHUR. Ueber eine neue Methode zur gemeinsamen Bestimmung von Kohlenstoff, Wasserstoff und Quecksilber in organischen Quecksilberverbindungen: Ber. Deut. chem. Gesell., Jahrg. 47, 1914, pp. 2935–2938.

Describes an open-tube method for the simultaneous determination of C, H, and Hg in organic preparations; distillation is accomplished in current of O_2 gas, and the Hg is collected on Au leaf or wire.

100. MARSH, J. E., and LYE, O. G. The quantitative estimation of mercury in organic compounds: Analyst, vol. 42, 1917, p. 84.

To prevent distillation of tarry matter when distilling mercury from organic compounds with lime, an admixture of two parts dry calcium sulphate is found to be effective.

DISTILLATION IN A TUBE SEALED AT ONE END.

101. ROSE, H. Ueber die quantitative Bestimmung des Quecksilbers und über die Trennung desselben von anderen Metallen: Pogg. Ann., Bd. 110, 1860, p. 529.

Hg compounds mixed with CaO are distilled in a combustion tube, and the Hg is collected under water. This method is described in most of the standard texts on quantitative analysis.

102. ATTWOOD, GEO. Quantitative assay of the ores and compounds of mercury by the blowpipe: Jour. Chem. Soc. London, vol. 35, 1879, pp. 207–212.

Describes various designs of small retorts of glass or steel used for the distillation of Hg compounds with litharge. The Hg is condensed under water. Amalgams also distilled. (See König, No. 96.)

103. FRANÇOIS, MAURICE. Dosage de mercure en présence de l'iode: Jour. Chim. Pharm., vol. 29, 1894, pp. 493–497; vol. 30, 1894, ——.

Hg may be determined in the presence of I by Rose's method (see No. 101) if soda lime is used as reagent. I can readily be determined in the residue.

ESCHBAUM, F. 1900. (See No. 3.)

Describes a step in final collection of precipitated Hg.

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104. RAASCHOU, P. E. Eine mikrochemische Quecksilberbestimmungsmethodes: Ztschr. anal. Chem., Jahrg. 49, 1910, pp. 172–204.

Describes a microchemical method, in which HgS is distilled in a tube with $PbCrO_4$, and the drop of Hg measured.

105. BERKHOUT, J. D. Quecksilberbestimmung in rauschswachem Pulver: Ztschr. ges. Schiess-Sprengstoffw., vol. 7, 1912, pp. 67–69.

Determines Hg in smokeless powders by evaporating an acetone solution of the powder with CuO and distilling the product in a closed tube with four small bulbs as condensers. The distilled Hg is measured under a microscope or weighed.

106. THORNHILL, E. B. Recovery of mercury from amalgamation tailing, Buffalo mines, Cobalt: Trans. Am. Inst. Min. Eng., vol. 52, 1916, p. 165; Met. and Chem. Eng., vol. 13, 1917, p. 896.

Describes a method of assaying tailings from an amalgamation mill, by distillation in closed glass tube with Fe filings, and collection of the Hg on Au beads in dilute KCN solution.

DISTILLATION IN A CRUCIBLE COVERED BY A COOLED GOLD OR SILVER TOP.

107. ESCHKA, A. Beschreibung des Verfahrens zur Bestimmung des Quecksilbers in seinen Erzen: Oest. Ztschr. Berg.-Hüt., Jahrg. 20, 1872, pp. 67–68; abstracted in Ztschr. anal. Chem., Jahrg. 11, 1872, pp. 344–345.

Distills Hg in a porcelain crucible with a concave Au cover. Results with known cinnabar and metallic Hg charges run low (from 0 to 6 mg.). (Eschka apparently used a balance sensitive to not less than 0.5 mg.)

108. TEUBER, E. Qualitative Probe auf Quecksilberspuren: Oest. Ztschr. Berg.-Hüt., Jahrg. 27, 1879, p. 423.

Describes a modification of the cover of the Eschka crucible to adapt it to the detection of minute quantities of Hg (as little as 0.1 mg.).

109. ZDRÁHAL, A. Die Eschka'sche Quecksilberprobe und ihre Genauigkeit: Oest. Ztschr. Berg.-Hüt., Jahrg. 29, 1881, pp. 485–487.

States that the Eschka method may be adapted to bituminous ore by washing the Hg deposit with alcohol, or, better, by destroying organic matter by an admixture of minium in the ore.

110. HAUSAMANN, OSCAR. Zur Eschka'schen Quecksilberprobe: Oest. Ztschr. Berg.-Hüt., Jahrg. 29, 1881, p. 561; Chem. Zentralb., 1881, p. 793.

Instead of Pb_2O_3 (see Zdráhal, No. 109), $PbCrO_4$ is recommended as oxidizer for high bituminous ores in Eschka method.

111. KROUPA, G. Notigen zur Quecksilberbestimmung nach A. Eschka: Berg.-Hüt. Jahrb. k. k. Bergakad. Loeben und Pribram, Bd. 37, 1889, pp. 369–388. Abstract in Berg.-Hüttenm. Ztg., Jahrg. 49, 1890, p. 150.

Describes modification of Eschka method for ores containing bituminous matter. Instead of Fe filings, thoroughly oxidized hammer slag (Fe_3O_4) and ZnO are used.

112. CHISM, R. E. Abänderung der Eschka'schen Quecksilberprobe: Berg.-Hüttenm. Ztg., Jahrg., 58, 1899, pp. 149–150.

The use of Ag instead of Au in the Eschka determination.

113. JANDA, F. Die Ermittlung des Quecksilbers in schwefelantimon- und-schwefelarsenhaltigen Quecksilberfahlerzen mittels der Golddeckelprobe: Oest. Ztschr. Berg.-Hüt., Jahrg. 47, 1899, pp. 205–208.

Describes modification of Eschka's method and of Kroupa's modification, using MnO_2 or $PbCrO_4$ and Na_2CO_3 in addition to the former's iron scale and ZnO. Designed to meet presence of As and Sb sulphides. States that duplicate analyses check well.

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114. EHRMANN, C., and SLAUS-KANTSCHIEDER, J. Ueber dalmatinische Quecksilbererze und deren chemische Untersuchung: Chem. Ztg., Jahrg. 26, 1902, pp. 201–202.

States that good agreement was not obtained in duplicate determinations by the Eschka method with pyritic ores, for example:

	Eschka gravity.	Gravity as HgS.
Ore 1	1.32 to 1.39	1.45
2	1.23 to 1.53	1.49

As dry fluxes there were used PbO, AnO, iron powder or MnO_2, MnO_2 with Na_2CO_3.

115. BIEWEND, R. Mittheilungen aus dem Probirlaboratorium, die trockene Quecksilberprobe: Berg.-Hüttenm. Ztg., Jahrg. 61, 1902, pp. 441–445.

Gives an account of the Eschka method, historical and critical, with several suggestions for improving the technique of the process. The original use of the Eschka method is attributed to Dr. Jordan at Clausthal before 1836.

116. WHITTON, W. W. The determination of mercury in ores: Calif. Jour. Tech., vol. 4, September, 1904, pp. 33–39.

Describes an iron crucible and cup for the Eschka determination. Gives results of numerous analyses.

117. HOLLOWAY, G. T. The assay of mercury ores: Analyst, vol. 31, 1906, pp. 66–71: Eng. and Min. Jour., vol. 83, 1907, p. 712.

Endorses the use of Ag instead of Au in the Eschka determination.

118. JAMES, G. A. The James apparatus for quicksilver determination: Eng. and Min. Jour., vol. 90, 1910, pp. 800–801.

Describes a modification of the Eschka method, using a nickel crucible and silver water-cooled cover.

118a. DE RUBIES, S. P. Exact and rapid method for the estimation of mercury in most of its compounds. Anales. Soc. expan. fis. quin., vol. 16, 1918, pp. 661–689; Chem. Abs., vol. 13, pp. 1982–1984.

Barium peroxide and carbonates of potassium barium and magnesium are used as reagents in the Eschka method. Applied to numerous organic compounds.

MISCELLANEOUS.

METHODS OF SOLUTION OF MERCURY-BEARING MATERIALS.

HEMPEL, C. W. 1858. (See No. 84.)

Describes method for obtaining chloride solution free from nitrates.

HEMPEL, C. W. 1859. (See No. 72.)

HgCl is dissolved by KI and I_2.

PERSONNE, M. J. 1863. (See No. 43.)

Mercury is dissolved by treatment with alkaline solution and Cl_2 gas.

VOLHARD, J. 1878. (See No. 51.)

HgS dissolved by Na_2S and NaOH solution.

119. RISING, W. B., and LENHER, VICTOR. An electrolytic method for the determination of mercury in cinnabar: Jour. Am. Chem. Soc., vol. 18, 1896, pp. 96–98.

HgS is dissolved by 20 per cent HBr solution.

FARUP, P. 1900. (See No. 8.)

Zn amalgam is dissolved by HCl and $KClO_3$.

120. MONTANARI, C. Determinazione industriale del mercurio nei minerali cinabriferi poveri col metodo di I. Personne: Gazz. chim. ital., vol. 33, pt. 1, 1903, pp. 155–160.

Ores are attacked by aqua regia, a special apparatus being used to prevent loss of Hg in the vapors.

RUPP, E. 1905. (See No. 11.)

Gives method for preparing an alkaline solution of K_2HgI_4.

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de Marignac, C. 1849. (See No. 32.)

Describes method for ignition of Hg nitrates or nitrites to HgO.

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LIST OF AUTHORS.

Name.	Ref. No.
Abelman, A.	99
Andrews, L.	64, 70
Archetti, A.	60
Attwood, G.	102
Berkhout, J. D.	105
Biewend, R.	115
Birkner, K.	28
Böttger, W.	42
Bressanin, G.	71
Brown, L. A.	13
Browning, K. C.	124
Carnot, A.	44
Castanares, A. P.	29
Cazeneuve, P.	37
Chism, R. E.	112
Cohn, R.	87
Deniges, G.	86
de Rubies, S. P.	118a
Dory, A.	122
Duccini, C.	15
Ebler, E.	14, 82
Ehrmann, C.	114
Elliott, J. A	4a
Erdmann, O. L.	94
Eschbaum, F.	3
Eschka, A.	107
Evesque, E.	45
Faktor, F. J.	25
Farup, P.	8
Feit, W.	9
Feldhofen, A.	22
François, M.	2, 103
Frank, F.	28
Fürbringer, P.	97
Goy, S.	67
Grüter, R.	80
Haehn, H.	123
Hager, H.	17
Hannay, J. B.	47
Haswell, A. E.	57
Hausamann, O.	110
Heinzelmann, A.	91
Hempel, C. W.	72, 84
Hilger, A.	36
Holloway, G. T.	117
James, G. A.	118
Jamieson, G. S.	59, 59a
Janda, F.	113
Jannasch, P.	98
Jolles, Adolph	1
Jones, C.	49
Jung, W.	7, 90
Kilpi, S.	26
Knovenagle, E.	14
Knox, J.	53
Kof, K.	123
Kolb, A.	22
König, C. R.	96
Krauss, L.	52, 75
Kroupa, G.	62, 111
Laborde, J.	21
Lahache, J. E.	45
Lehman, F.	31, 77, 79
Lehnert, H.	98
Lenher, V.	119
Lescoeur, H.	65
Liebig, J.	54
Litterschied, F. M.	40
Liversedge, S. G.	30
Löwe, J.	23
Lye, O. G.	100
McBride, R. S.	27
Marchand, R. F.	94
de Marignac, C.	32
Marsh, J. E.	100
Méniere, M. P.	93
Mohr, C. F.	88
Montanari, C.	120
Morawitz, H.	50
Muller, J. A.	76
Namias, R.	6
Neison, E.	48
Neubauer, C.	97
Nöll, P.	121
Norton, J. T.	73
Oddo, B.	55
Pazourek, E	56a
Personne, M. J.	43
Peters, C. A.	38
Pretzfeld, C. J.	39
Procter, H. R.	92
Raaschou, P. E.	104
Randall, D. L.	85
Reichard, C.	10
Reinthaler, F.	81
Renk, ——.	35

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Name.	Ref. No.
Richards, T. W.	4
Riesser, O.	18
Rimini, E.	66
Rising, W. B.	119
Robertson, P. W.	41
Rose, H.	5, 19, 101
Rupp, E.	11, 31, 52, 68, 69, 74, 75, 77, 79, 121
Scherer, J. J.	34
Schirmer, W. F.	69
Schumacher, ——.	7, 90
Seamon, W. H.	46
Seymour-Jones, A.	92
Singer, S. K.	4
Slaus-Kantschieder, J.	114
Smith, C. E.	12
Stüwe, W.	83
Teuber, E.	108
Thornhill, E. B.	106
Treubert, F.	20
Tuson, R. V.	48
Utz, F.	61–70
Vanino, L.	28
Vignon, L.	89
Vitali, D.	63
Vohl, H.	33
Volhard, J.	24, 51
von Bonsdorff,	16
von Jüptner, H.	58
von Raumer, E.	36
Votocek, E.	56, 56a
Wandesleben, ——.	95
Wegelius, H.	26
Whitton, W. W.	116
Zdrahal, A.	109

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LIST OF SUBJECTS.

	Ref. No.
Gravimetric and precipitation methods	1–42
Precipitation of free mercury	1–15
By zinc	1–2
By copper	3–4a
By brass	98
By stannous chloride	5–8
By alkali arsenite	9–10
By formaldehyde	11–12
By chloral hydrate	13
By hydrazine or hydroxylamine	14–15
Precipitation of calomel	16–22
By organic reagents	16–18
By ferrous sulphate and alkali	57, 58, 85
By phosphorous acid	19–20
By stannous chloride	21
By sulphur dioxide	63
By hydrogen peroxide and ammonium tartrate	22
By sodium chloride	55
Precipitation of mercuric sulphide	23–29
Precipitation of mercuric iodide	30–31
Precipitation of ammonium derivatives	29, 47, 48, 49, 71
Other precipitates	32–42
Volumetric methods	43–89
Direct titrations	43–61
With potassium iodide	43–46
With potassium cyanide	47–50
With potassium thiocyanate	51–53
With stannous chloride	21
With sodium chloride	54–56
With sodium thiosulphate	34
With potassium permanganate	57–58
With potassium iodate	59, 59a
With ammonia	60–61
Indirect and residual titrations	62–88
Acidimetric	62–64
Alkalimetric	65–71
Idometric	72–83
By permanganate	84–85
By cyanide	86
By thiocyanate	87
By chloride	88
Colorimetric methods	89–93
As mercuric sulphide	89–92
As mercuric diphenyl carbazide	93
Distillation methods	94–118a
Distillation in a tube not sealed at either end	94–100
Distillation in a tube sealed at one end	101–106
Distillation in a crucible covered by a cooled gold or silver top	107–118a
Miscellaneous	119–124
Methods of solution of mercury-bearing materials	119–121
Other miscellaneous methods	122–124

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